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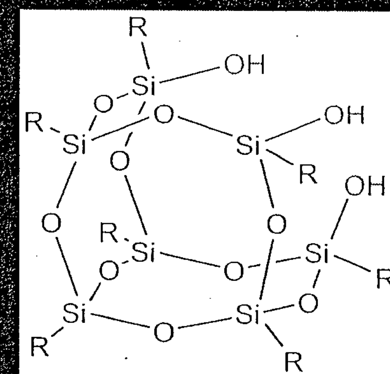
MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO) 22 February 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-037**
Rusty Blanski, "Molecularly Reinforced Polymers"

Minnesota Technology Forum **(Statement A)**
(Minnesota, 15 February 2002) **Deadline: PAST DUE)**

Molecularly Reinforced Polymers



Dr. Rusty L. Blanski
Polymer Working Group
Air Force Research Lab, Edwards

DISTRIBUTION STATEMENT A:
Approved for Public Release -
Distribution Unlimited

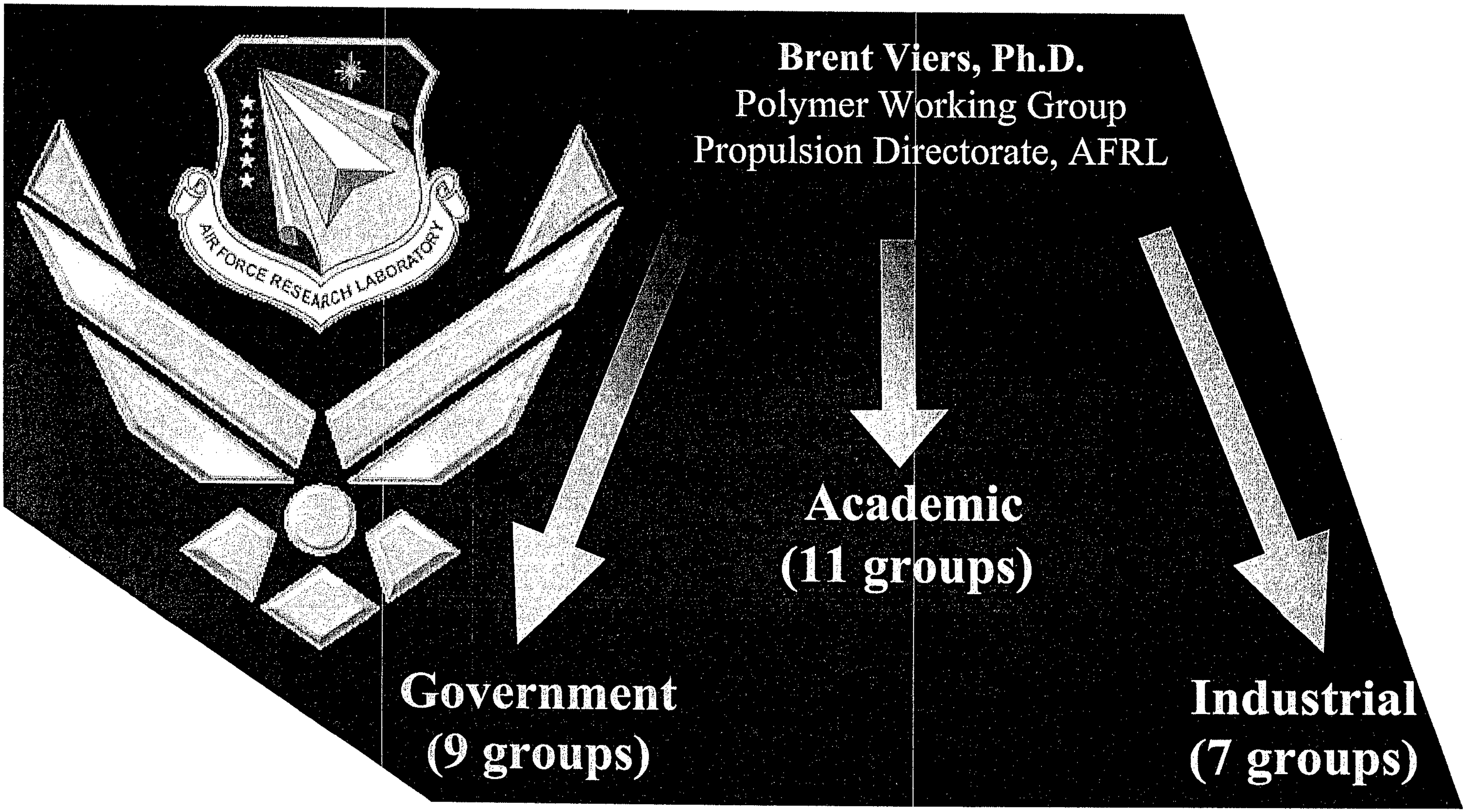
Timothy S. Haddad, Frank J. Feher, Brent D. Viers, Rene I. Gonzalez, Maj Steven A. Svejda, Joe Lichtenhan, Joe Schwab

Overview

- Introduction
- POSS Monomer Synthesis
- POSS Blends
- POSS Applications

POSS-Polymer Research is a Large Collaboration

Government-Academia-Industry



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Polymer Working Group

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Justin Leland
Pat Ruth
New Post-Doc: Polymer Synthesis

Edwards

Dr. Kevin Chaffee
Mr. Paul Jones

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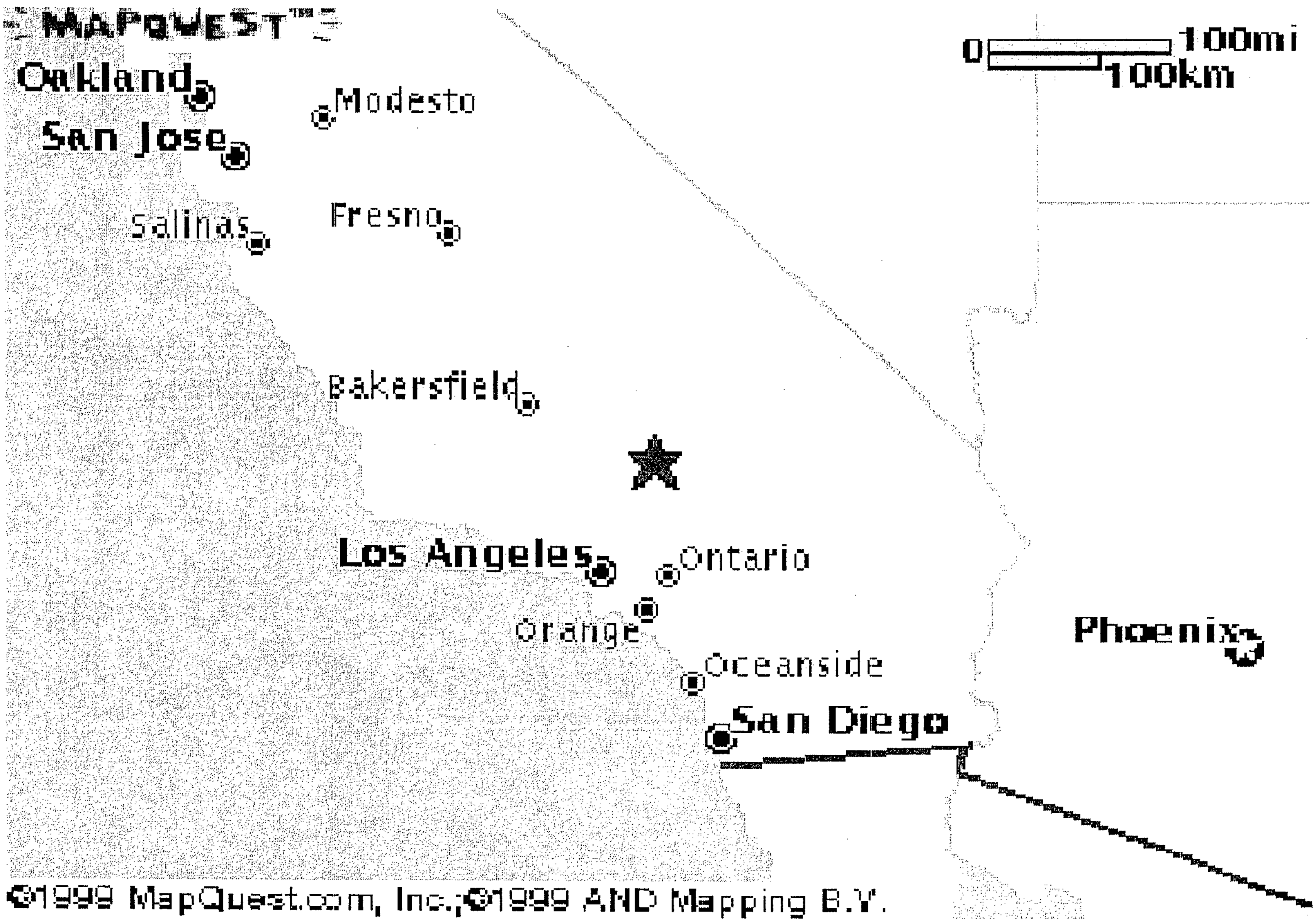
Prof. Andre Lee - MSU
Dr. Joe Lichtenhan - HP
Dr. Joe Schwab - HP
Prof. Pat Mather - UConn
Dr. Jeff Gilman - NIST
Prof. Ben Hsiao - SUNY SB
Prof. Bryan Coughlin - UMass
Prof. Gar Hoflund - UF
Dr. Barry Farmer - AFRL/MLBP
Dr. Rich Vaia - AFRL/MLBP
Dr. Seng Tan - WMR
Prof. Mark Gordon - Iowa St. U
Dr. Howard Katzman - Aerospace
Mr. Don Geidt/Mike Blair - CSD/Thiokol

Funding: AFOSR (Dr. Charles Lee), AFRL, Hybrid Plastics

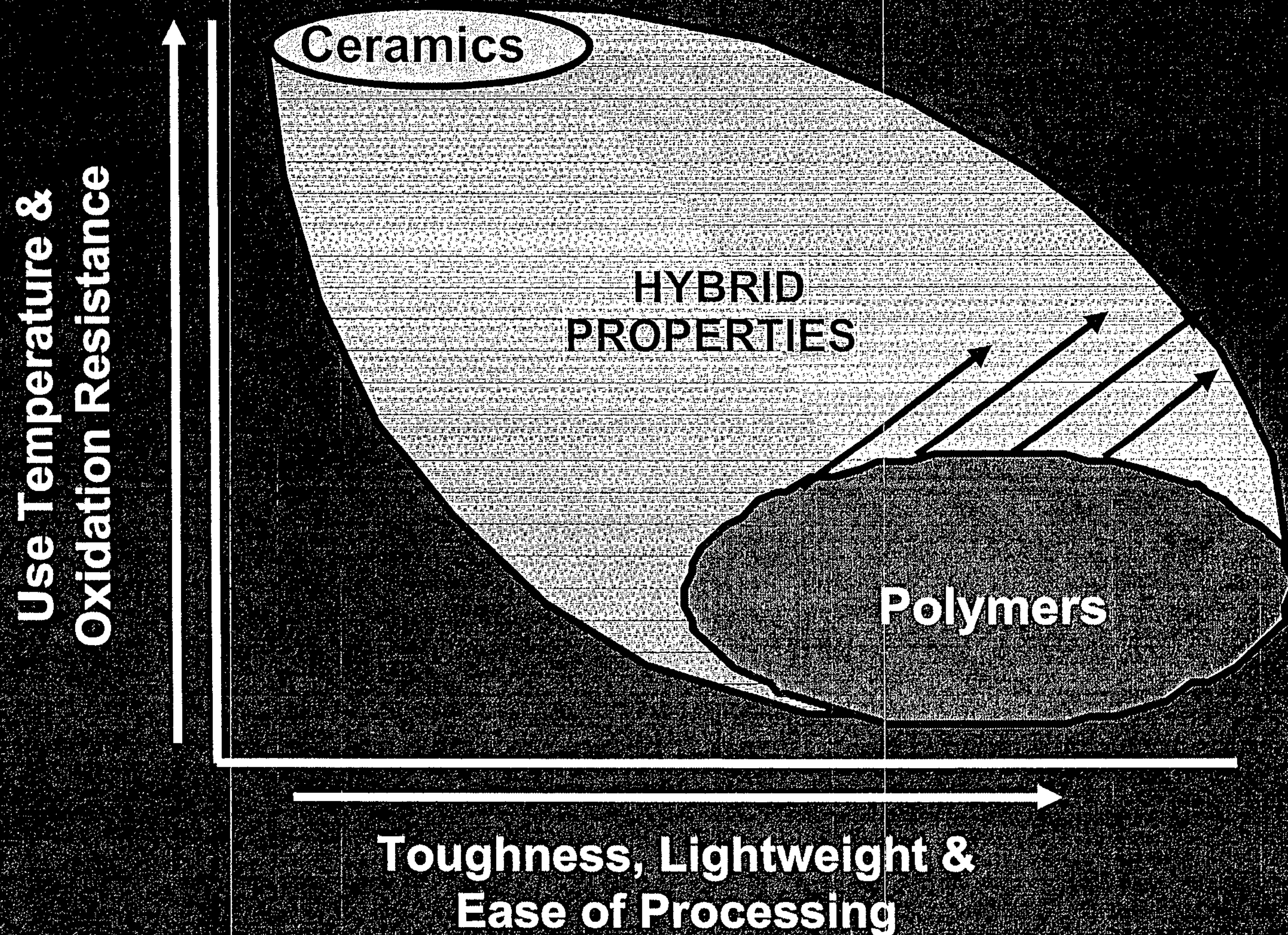
Basic R&D | Applications R&D

Air Force Research Laboratory

Located ~ 100 miles from LA



Multiple Applications/Multi-Function

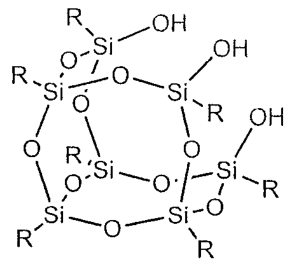


- Improve High Performance Polymers/ Transform Commodity Polymers into High performance Polymers
- Develop Multi-Functional Materials/ Replace Metal Parts with Polymers

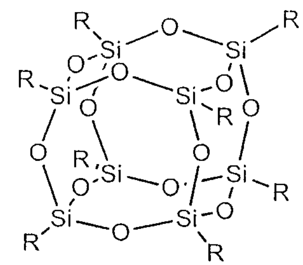
POSS = Polyhedral Oligomeric Silsesquioxane: General Synthesis

$RSiCl_3 + H_2O \longrightarrow$

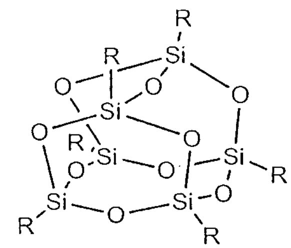
R =Cyclohexyl
Cyclopentyl
Cycloheptyl
Vinyl
Methyl



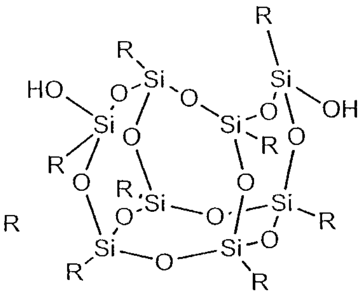
R = Cyclohexyl
Cyclopentyl
Cycloheptyl



R =Cyclohexyl
Cyclopentyl
Vinyl
Methyl



R = Cyclohexyl



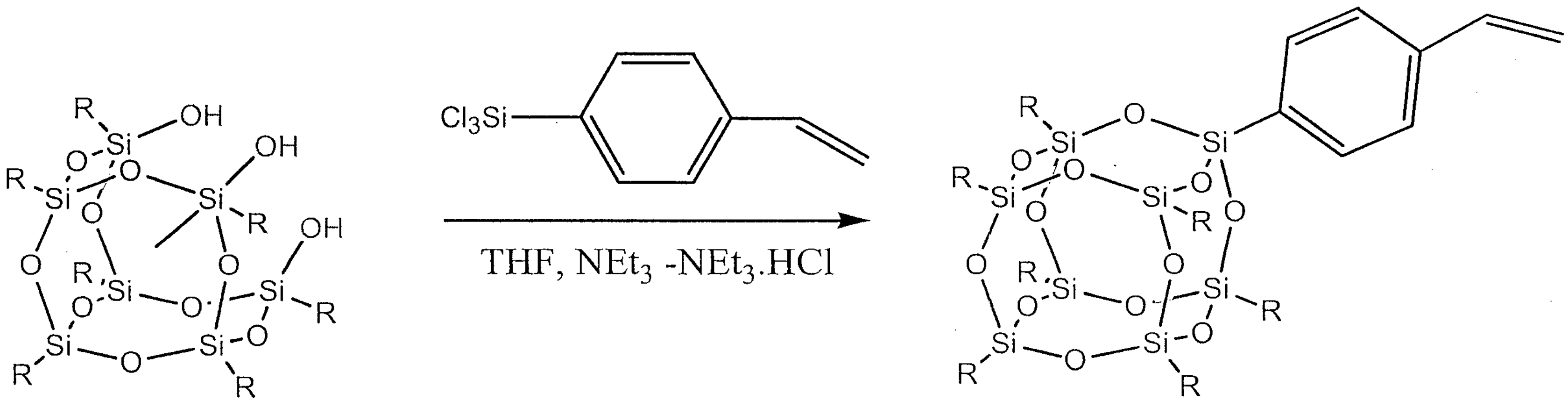
R = Cyclohexyl

R=Cyclohexyl: Brown and Vogt 1965
Feher, Newman, Walzer 1989
*** Lichtenhan (AFRL, mid '90's) Optimized Purification**

Cyclopentyl: Feher, Budzichowski, Weller, Blanski, Ziller 1990 (1991)
*** Lichtenhan (AFRL, 1993) Optimization**

All of these materials are colorless solids at ambient temp

POSS = Polyhedral Oligomeric Silsesquioxane: General Synthesis

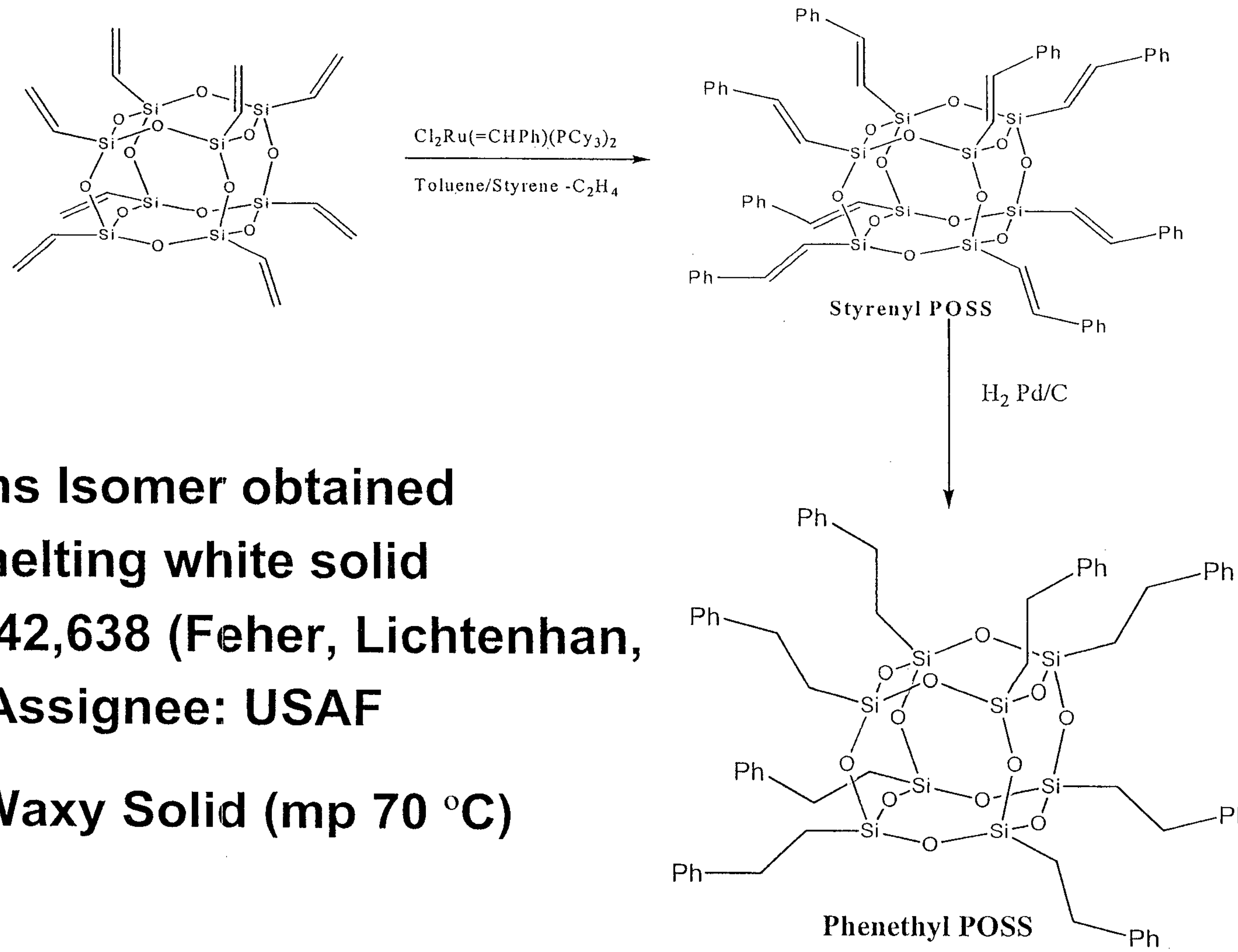


R = cyclopentyl

R = cyclopentyl

- Functionalized POSS Monomers for Polymerization in traditional systems (styryl, norbornyl, methacrylpropyl, etc.)

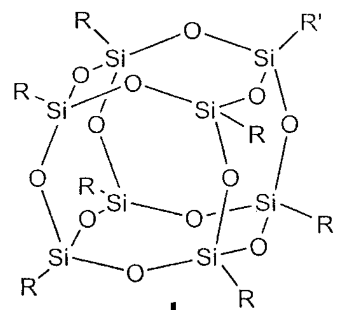
POSS = Polyhedral Oligomeric Silsesquioxane General Synthesis

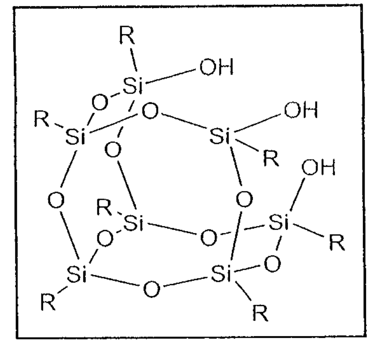


- All trans Isomer obtained
- High melting white solid
- US 5,942,638 (Feher, Lichtenhan, et al) Assignee: USAF

White Waxy Solid (mp 70 °C)

POSS Monomer/Polymer Trees





halides
alcohols
esters
acids
bisphenols
acid chlorides
aryldiacids

nitriles
amines
isocyanates
arylbisamines
arydiisocyanates

silanes
silanols
siloxanes

olefins
styryls
acrylics

norbornyls
cyclopropyls
epoxies

"POSS-technology is sustainable via dual-use markets"

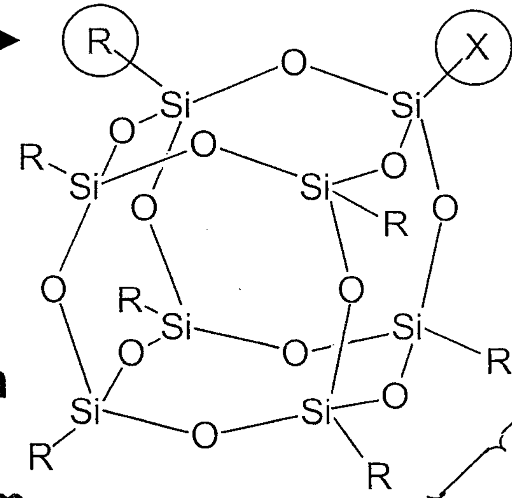
<u>>100 polymer systems</u>

- POSS-rubber*
- POSS-urethane*
- POSS-epoxy*
- POSS-phenolic*
- POSS-imide*

monomers and polymers.

Anatomy of a Polyhedral Oligomeric Silsesquioxane (POSS) Molecule

Nonreactive organic (R) groups for solubilization and compatibilization.



May possess one or more functional groups suitable for polymerization or grafting.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

Thermally and chemically robust hybrid (organic-inorganic) framework.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

The maximization of property enhancements in polymers results from interaction at the nano-level (Edwards AFRL/PRSM ---> POSS monomers)

Key Roadblocks for POSS Materials, Sept. 1998

- **Time for Production of POSS feedstocks**
- **Cost of POSS feedstocks/monomers/polymers**
- **Volume of POSS feedstocks/monomers**
- **Structure/Property Relationships**
- **Blends & Processing**

POSS™ Commercialization and Cost Reduction Campaigns

In October 1998 Hybrid Plastics and the Air Force Research Laboratory entered into a Cooperative Research and Development Agreement (CRADA) for the commercialization of POSS™ Nanotechnology.

Technical Objective:

- Commercialization of POSS™ Technology.

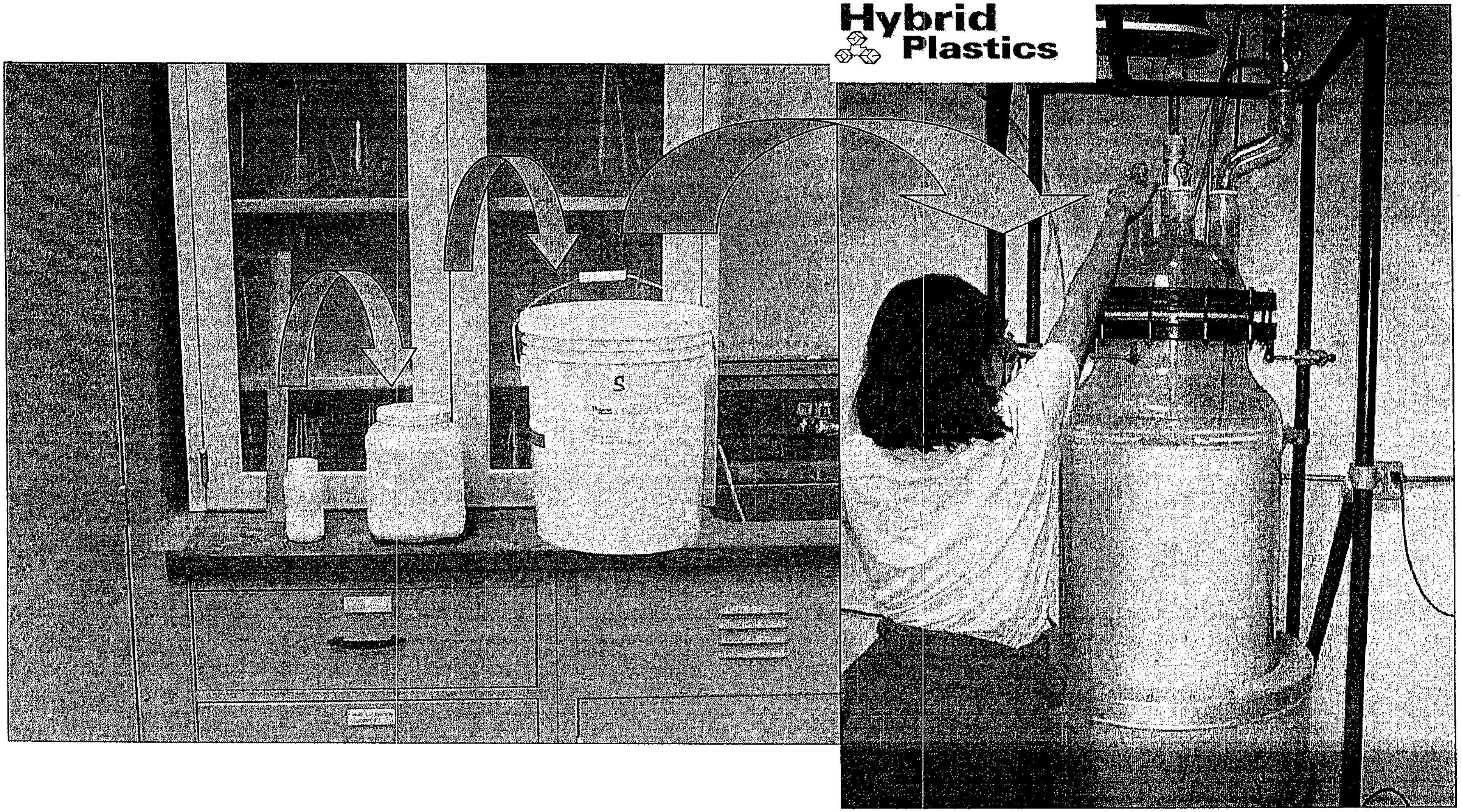
Also in October 1998 Hybrid Plastics was awarded a 3-year, $2 million grant by NIST's Advanced Technology Program (ATP) to reduce the cost of POSS Nanostructured™ Chemical Technology by a factor of 100.

Technical Objective:

- Reduce costs of POSS™ Technology from $1000-$5000/lb to $10-50/lb.

Hybrid Plastics

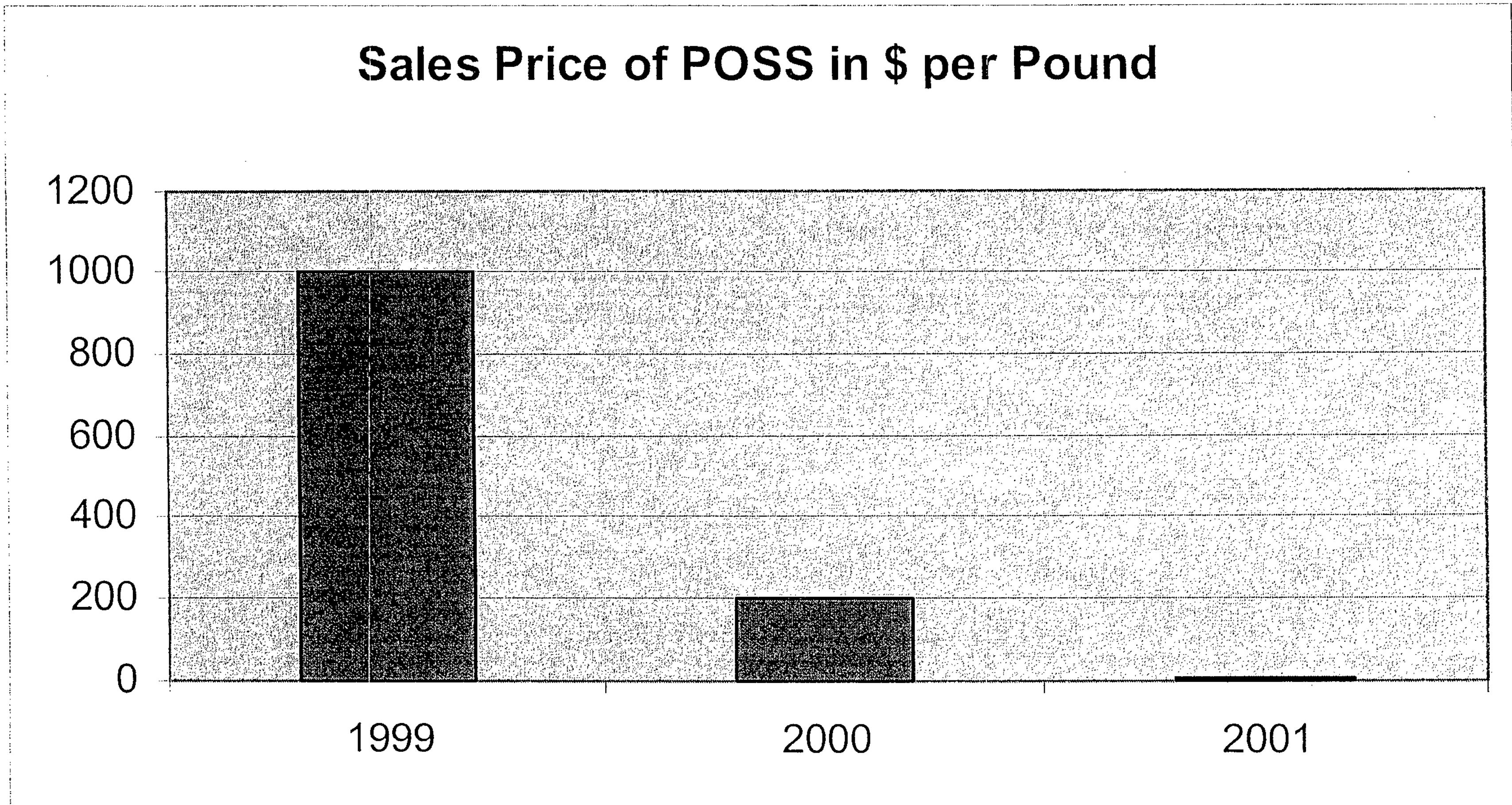
Technology Transfer = Scalability = Price Reduction, Sustainability



Time	1991	1994	1998	2000
Quantity	< 50g	2-5 lb	20-40 lb	> 400 lb
Price	???	$1000-5000/lb	$1000-5000/lb	$20-250/lb

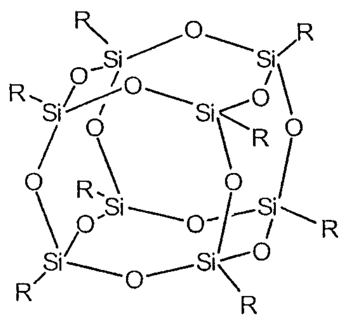
→ Plant

Retail Prices of POSS

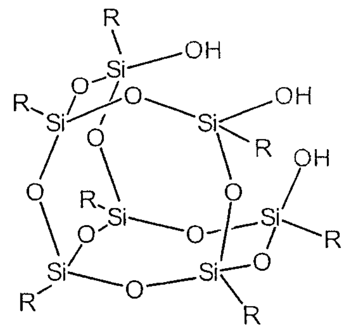


Hybrid Plastics™

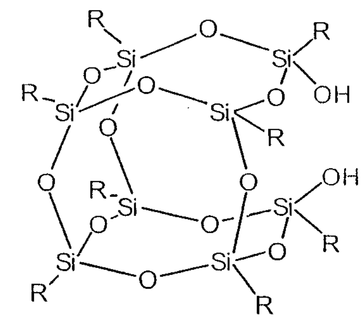
POSS Diversity



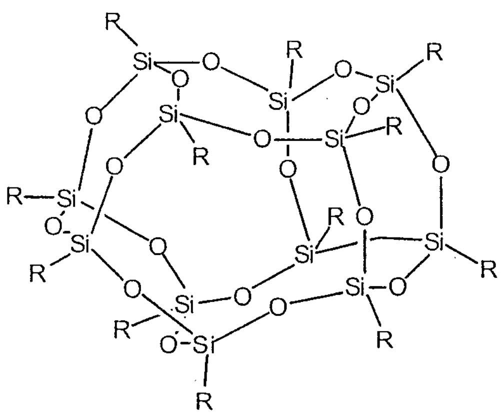
R = Methyl
Isobutyl
Cyclopentyl
Cyclohexyl
Isooctyl
Phenyl
Phenethyl
Octadecene



R = Isobutyl
Cyclopentyl
Cyclohexyl
Isooctyl
Ethyl



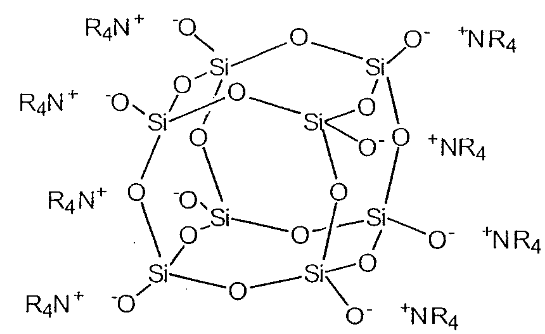
R = Isobutyl
Cyclopentyl
Cyclohexyl
Isooctyl



R = Phenyl
Trifluoromethylpropyl

Polydisperse Cages
(T_8, T_{10}, T_{12})

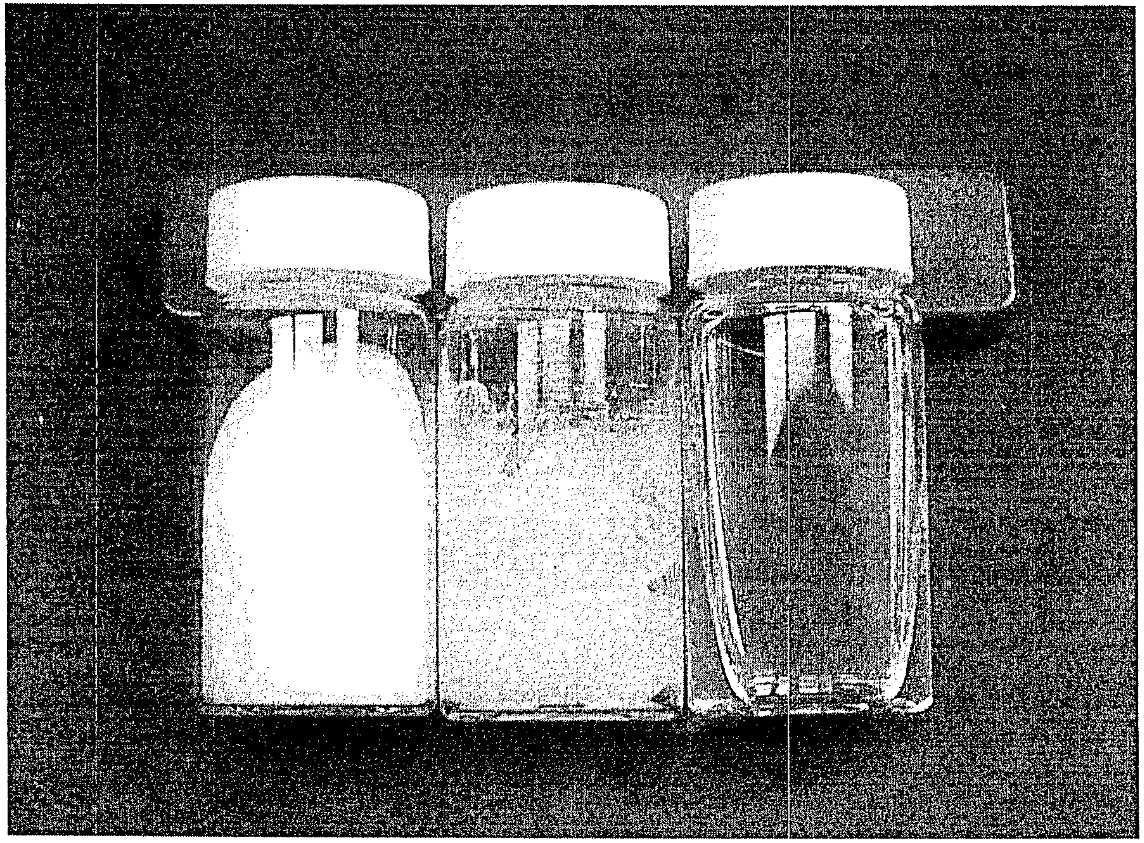
R = Vinyl
Phenethyl



R = Methyl

Hybrid Plastics

Nanostructured™ POSS Chemicals
Physical Form of Products



Crystalline Solids — Wide melting range 24°C to 400°C+

Waxes

Liquids & Oils — Wide viscosity range 40cSt. to 400cSt

Hybrid Plastics™

Global Sales of Nanostructured™ Chemicals

R&D chemical catalog sales (1997 to present)

Aldrich Chemical Company

Gelest Inc.

Trends in Hybrid Plastics' R&D/bulk chemical sales

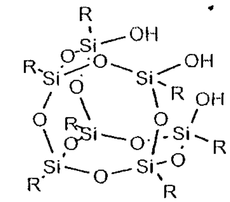
65% Asia and Europe

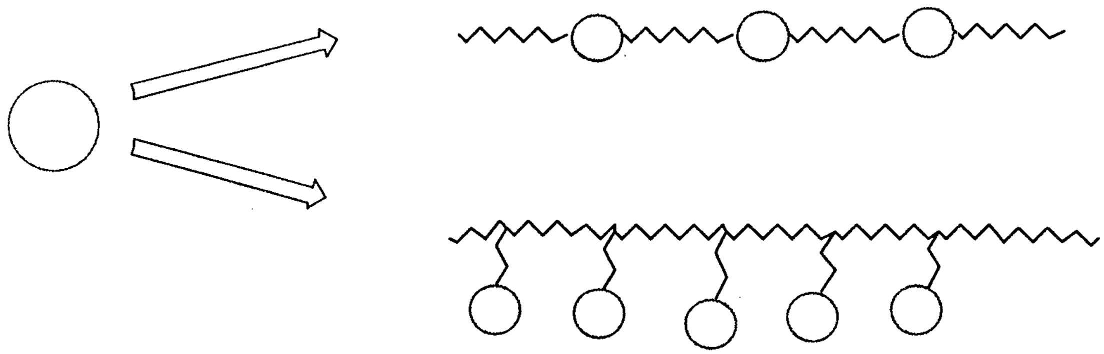
30% US Domestic

5% Government Sales

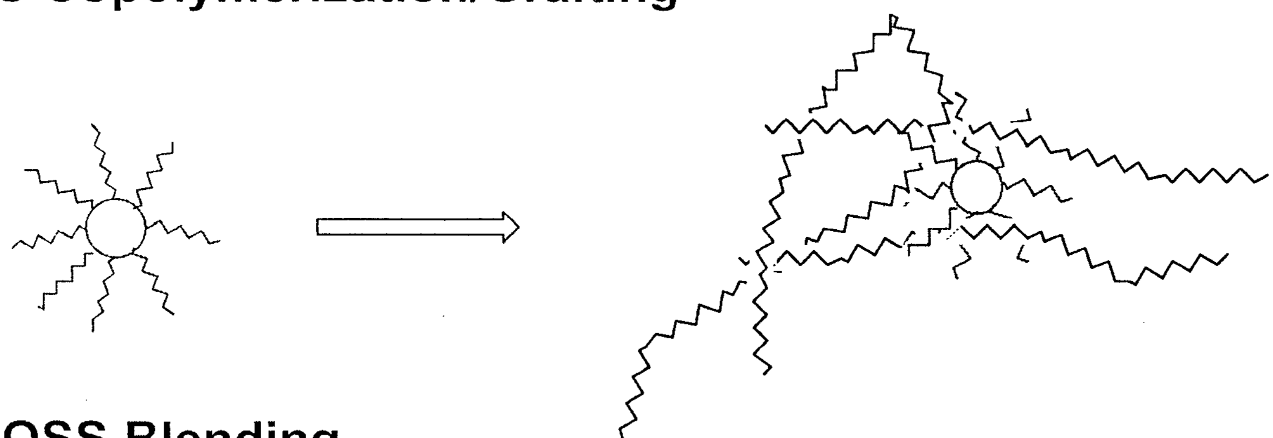
Hybrid Plastics™

POSS Polymer Incorporation





POSS Copolymerization/Grafting



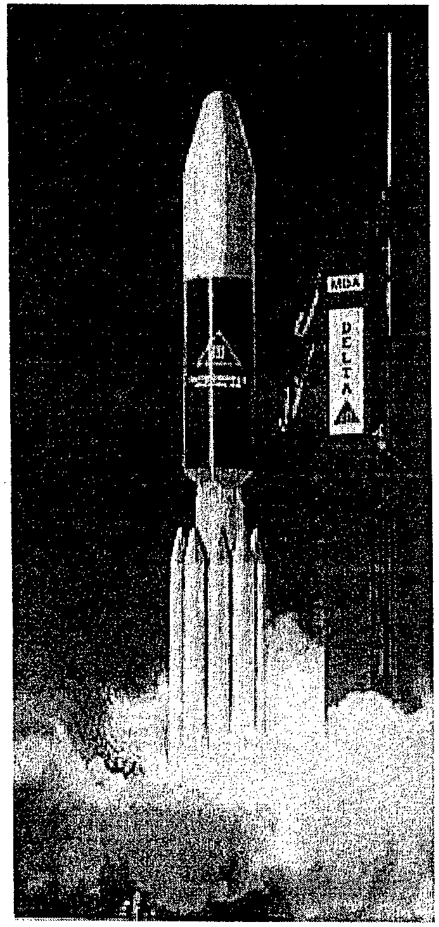
POSS Blending

Size & Shape

- improved mechanicals
- increased T_g, T_m, T_{dec}
- decreased creep
- improved processing
- optically transparent

POSS-Polymer Blends for Air Force Applications

- **GOAL: To increase the performance characteristics of polymers by blending in POSS**



<u>Potential Applications of POSS-Polymer Blends</u>

- **High Temperature Insulation for Solid Rockets Motors**
- **Capacitors**
- **Space-survivable Materials and Coatings**
- **Low/High Temp. Hybrid Lubricants**
- **Plastic Tubing and Ducting for Liquid Rockets Engines**
- **High Temperature/High Translation Strength Composites**
- **Improved Radome Materials**

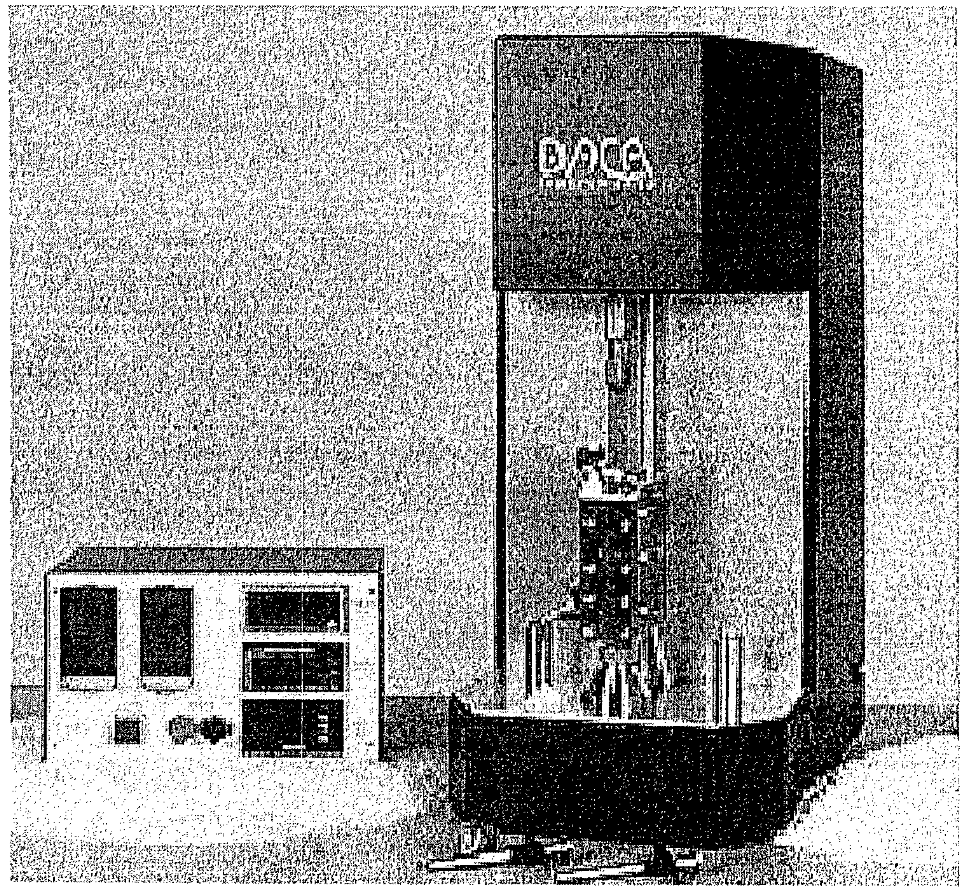
POSS-Polymer Blends
Why Use Blendables?

- Easier to tailor the organic side groups of the POSS molecule to give a polymer-compatible species
- Simple blending techniques can be used instead of copolymerization with reactive POSS monomers: decreased development time
- Potential Drop-in molecular modifier without requiring expensive replacement of processing equipment

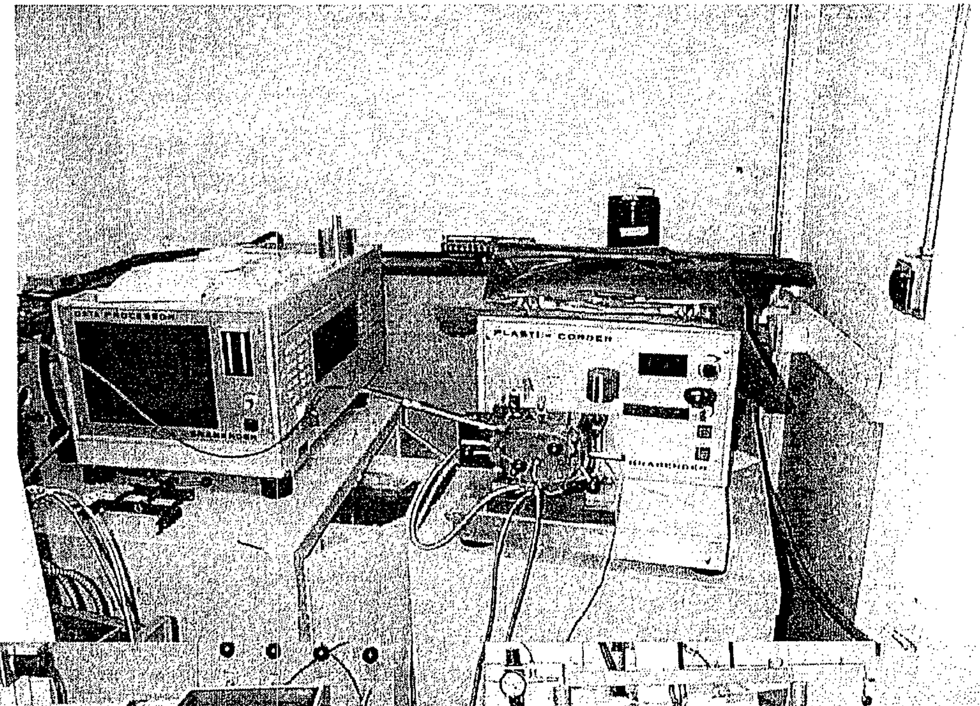
Preparation of Polymer- POSS Blends

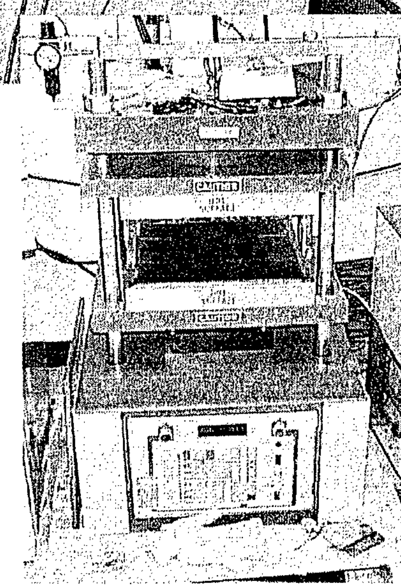
<u>Twin Screw Processing</u>

- Place Polystyrene in Extruder
- Add POSS
- Blend 2-5 Minutes
- Use a DACA for small scale (4 g)
- Very High Shear



Preparation of Polymer-POSS Blends





Traditional Processing:

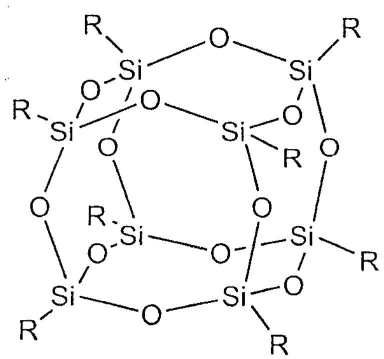
Brabender Mixer

- Place Polystyrene in Mixer at temperature
- Add POSS
- Blend 5-10 Minutes
- Grind
- Press into disks/extrude/ injection mold
- 60 gram scale

POSS Blends

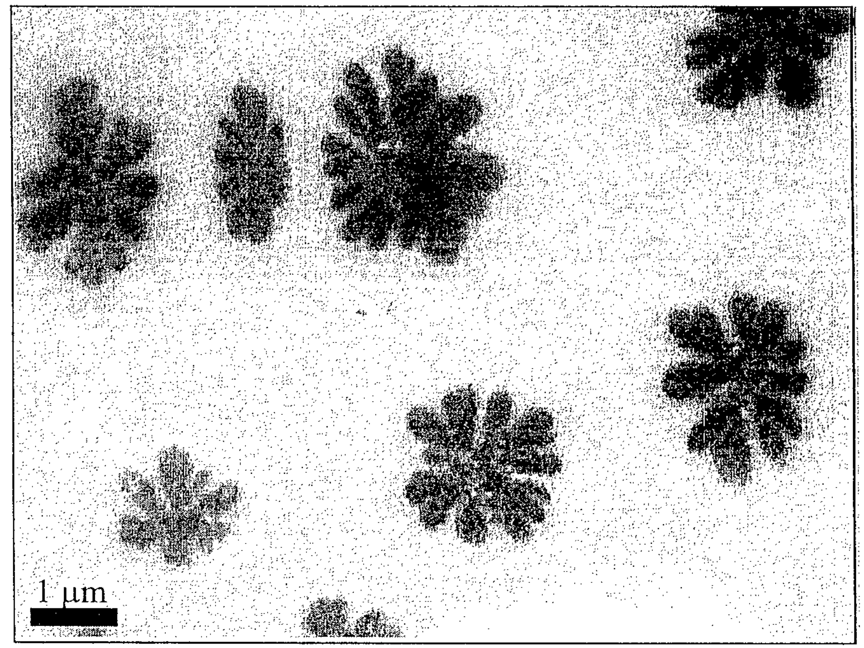
Importance of Organic Side Groups

50 wt % Cp_8T_8 in 2 million mol. wt. Polystyrene



R = cyclopentyl

Cp_8T_8

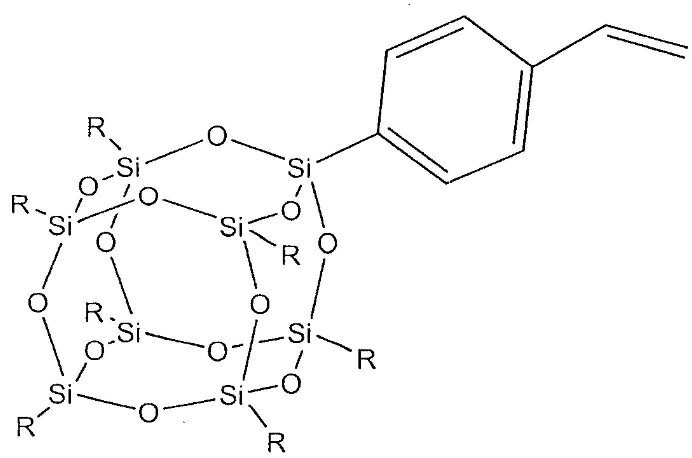


- **TEM image clearly shows formation of immiscible POSS crystallites (20-50k molecules)**
- **Film is Cloudy**

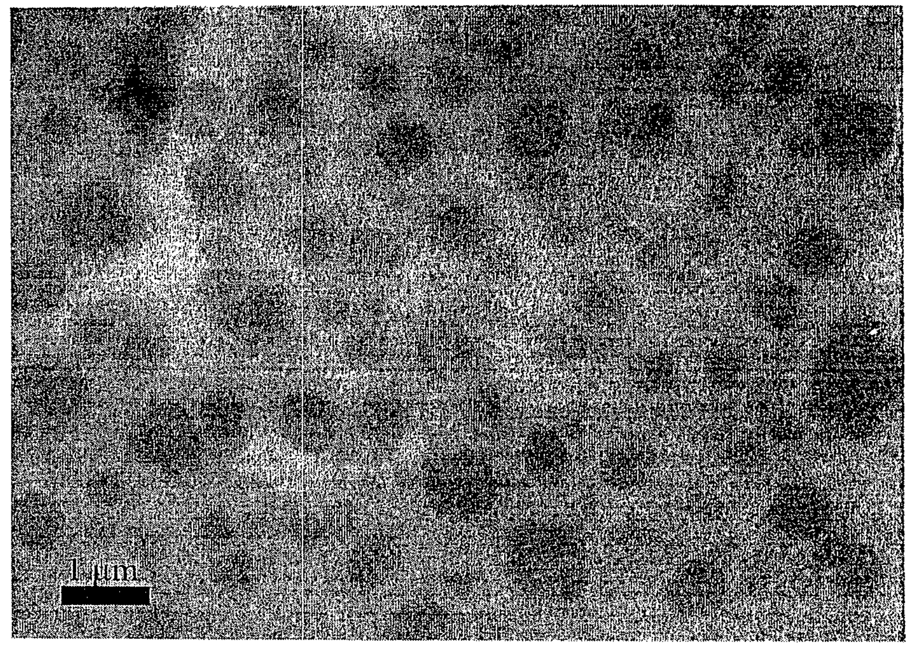
POSS Blends

Importance of Organic Side Groups

50 wt % Cp_7T_8Styryl in 2 million mol. wt. Polystyrene



R = cyclopentyl

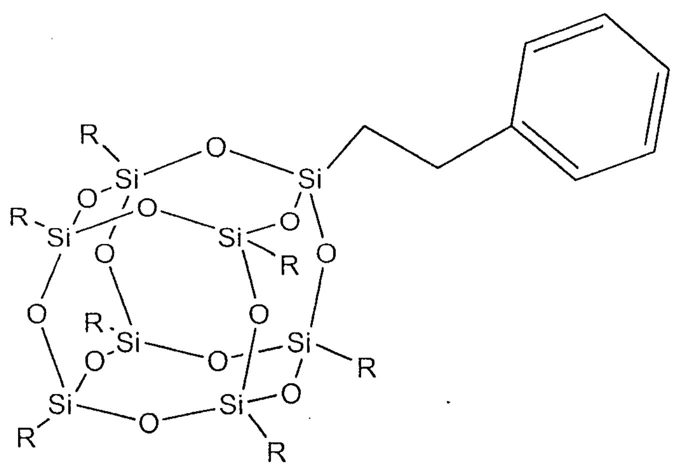


- TEM image shows significant decrease in size of crystallites
- Film is Cloudy

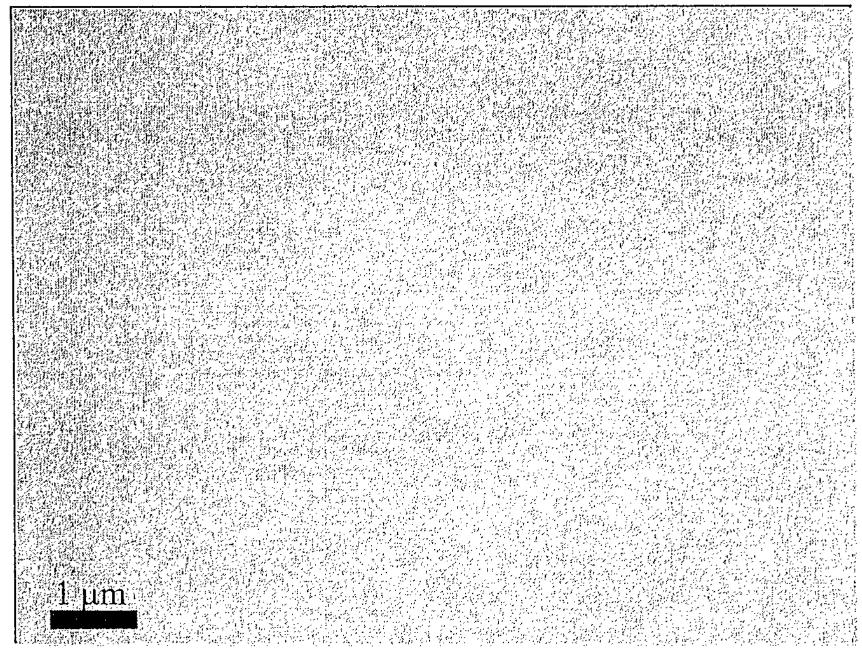
POSS Blends

Importance of Organic Side Groups

50 wt % Phenethyl$_8$T$_8$ in 2 million mol. wt. Polystyrene

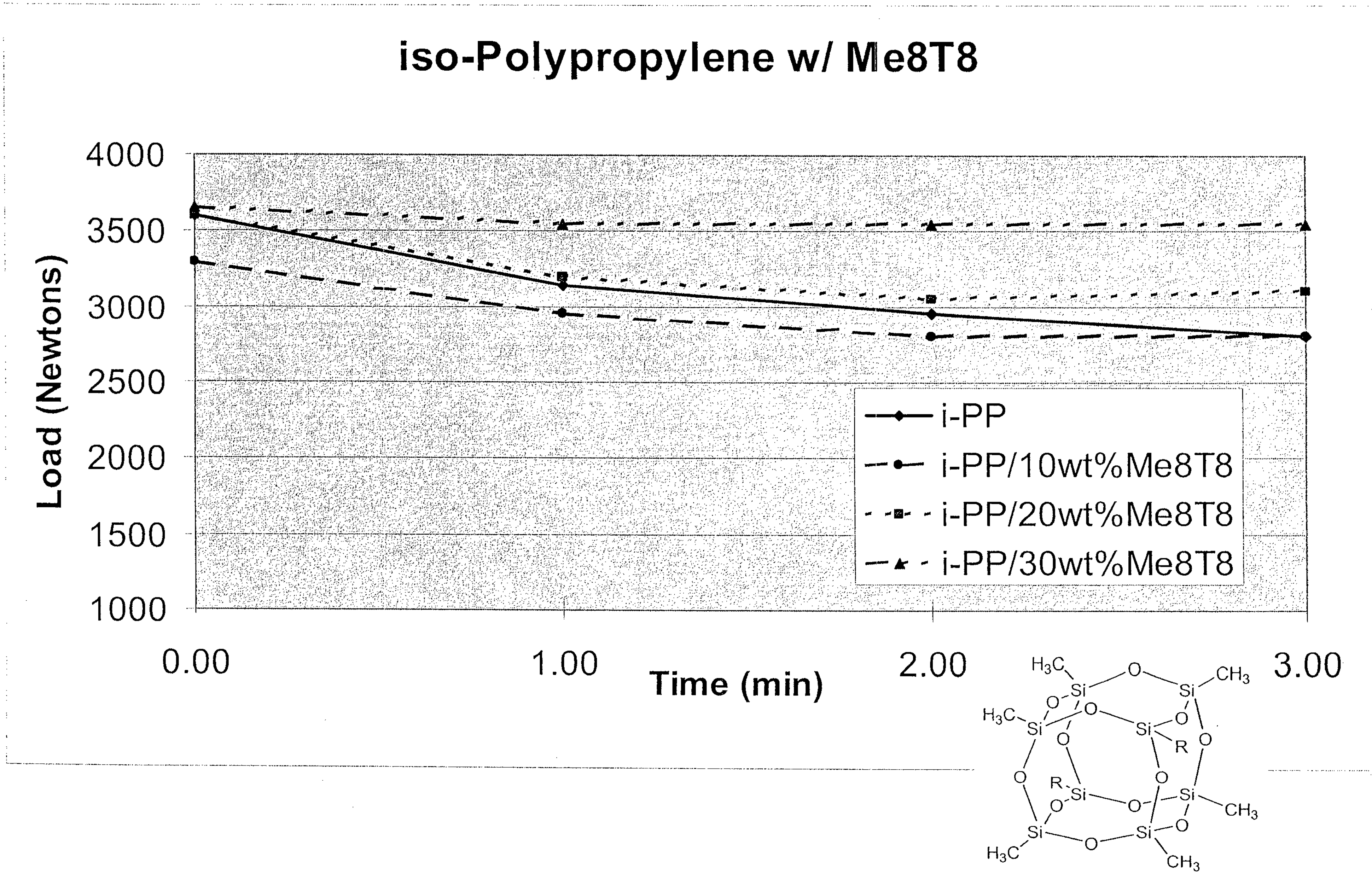


R = Phenethyl

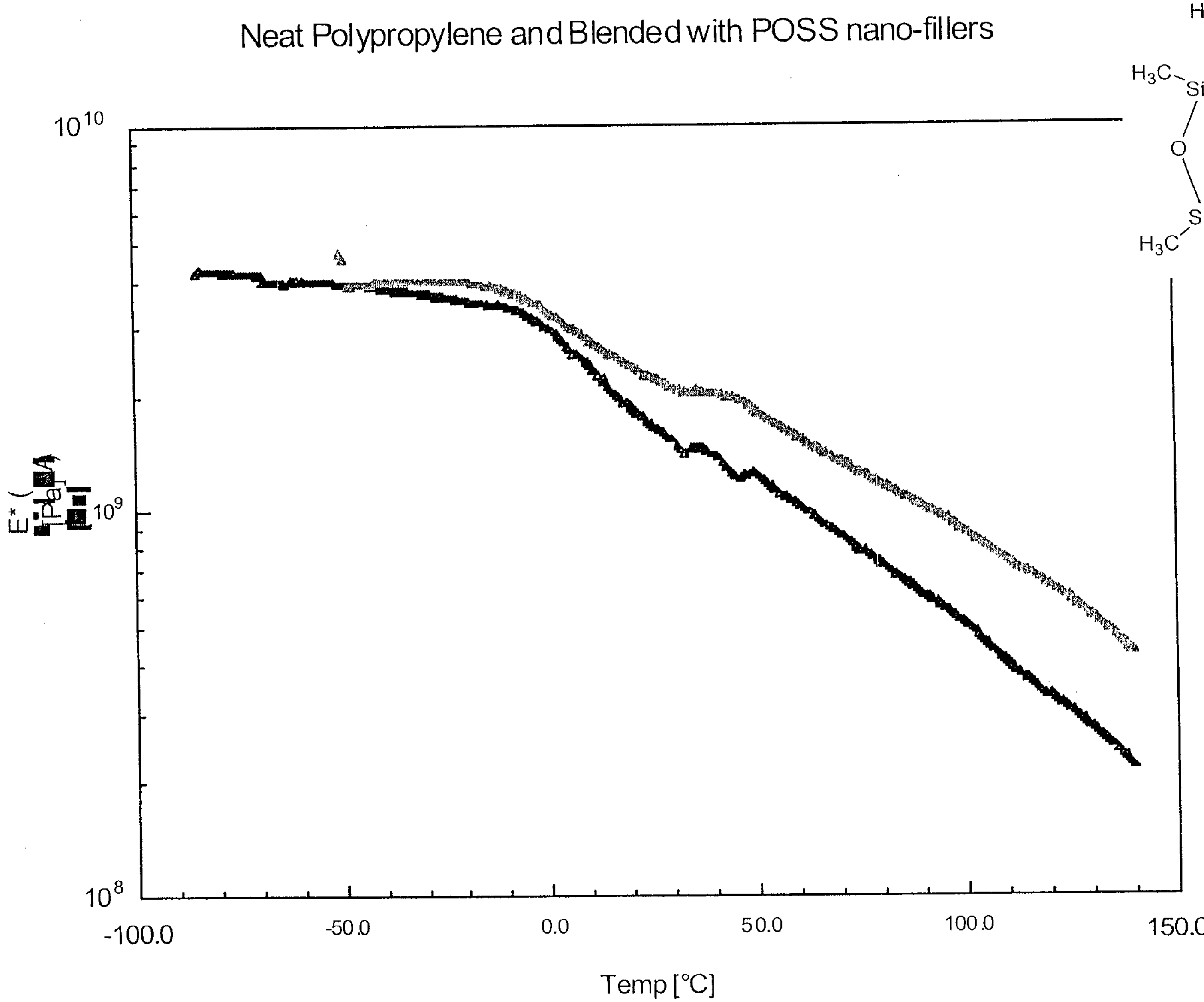


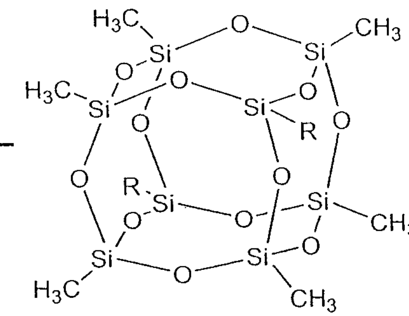
- Demonstrated Complete Compatibility!
- Grey domains represent miscible POSS/polystyrene
- Black dots are POSS crystallites (<100 POSS molecules)
- Film is Clear

i-PP/Me_8T_8 Processing Studies

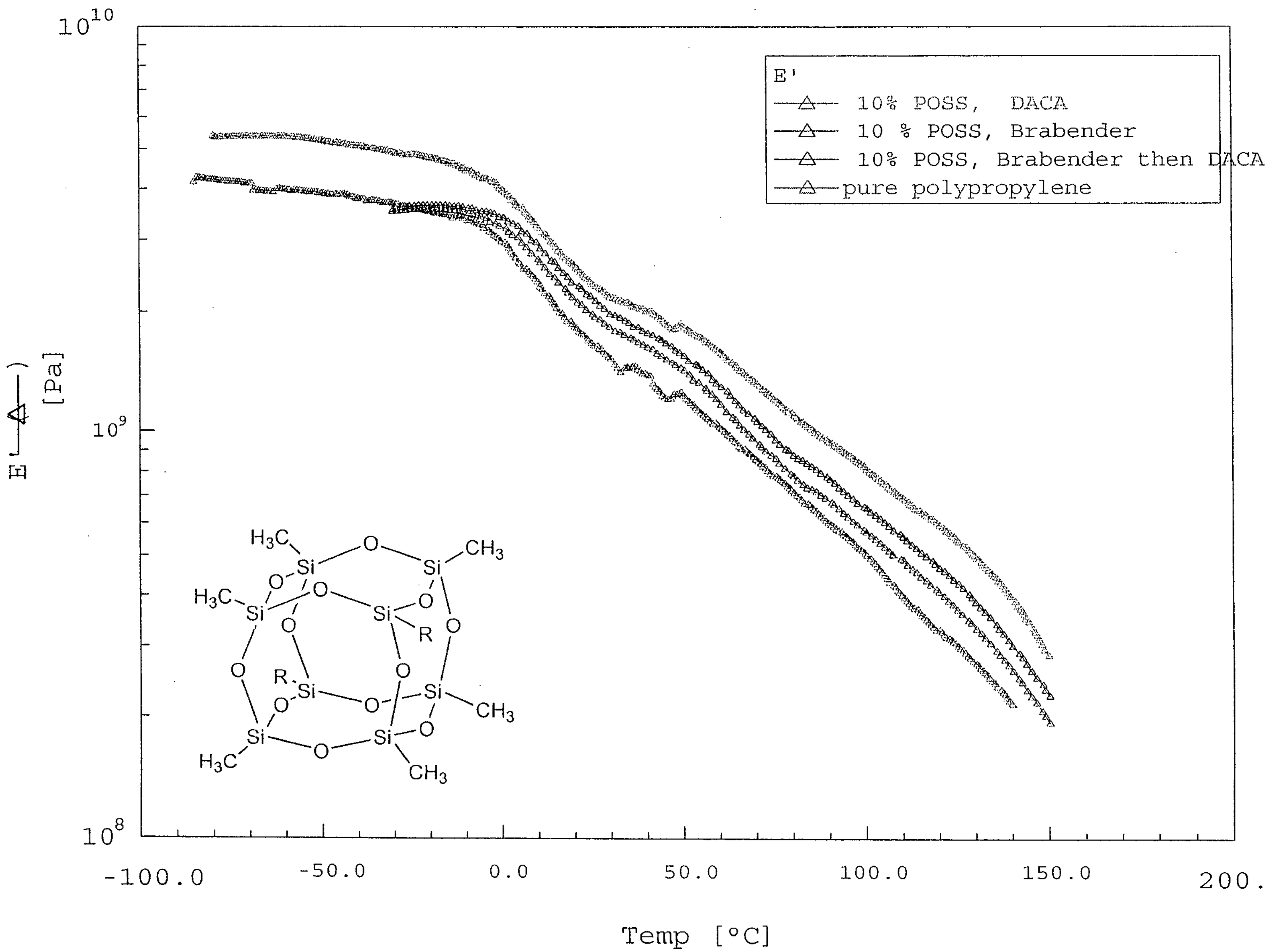


i-PP/Me_8T_8 Processing Studies



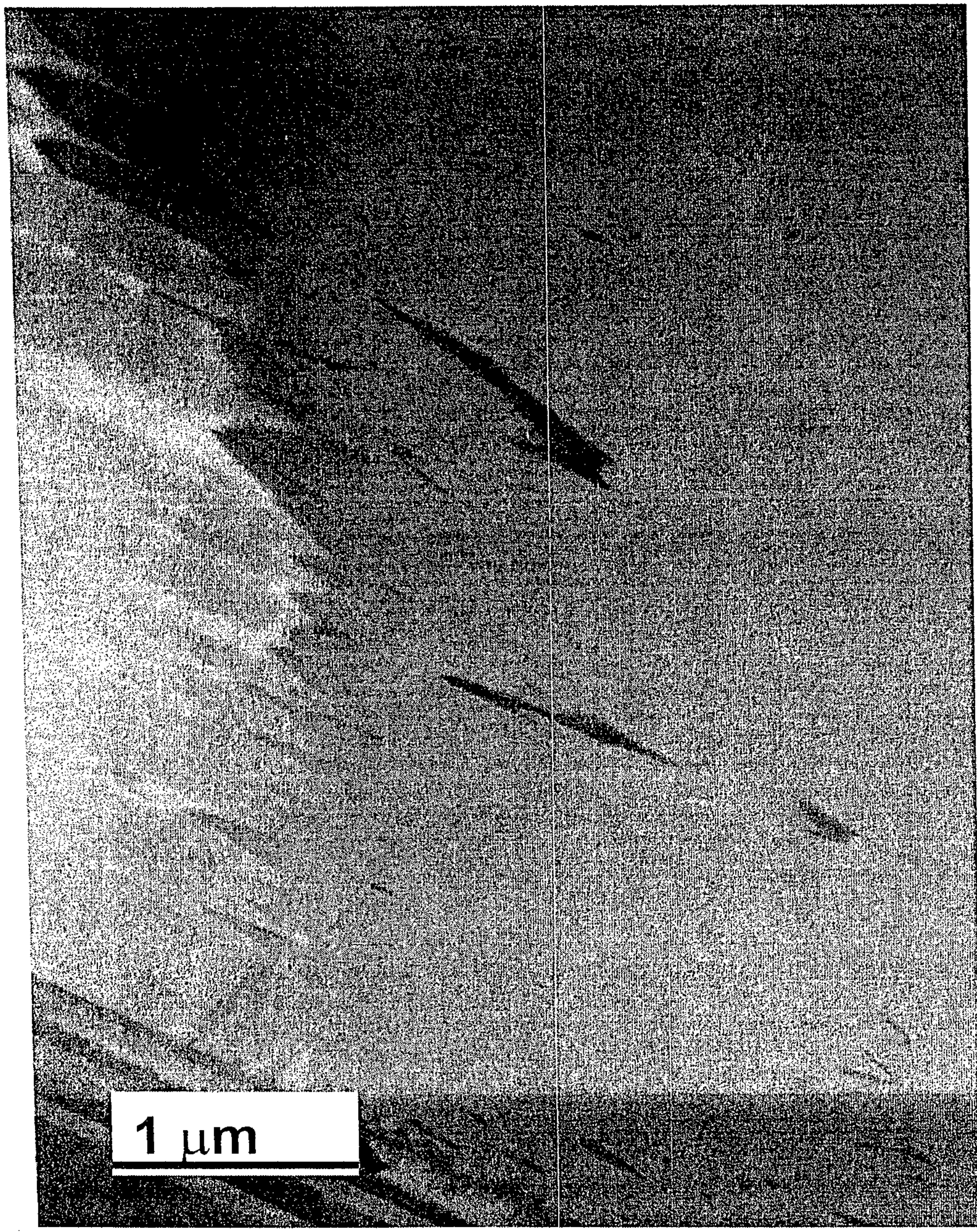


i-PP/Me_8T_8 Processing Studies



i-PP/Me_8T_8 Blends – Processing Issues

Brabender



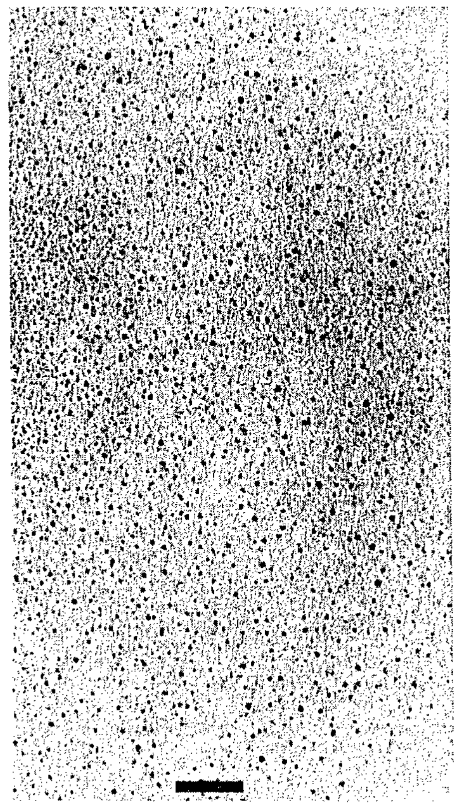
Twin-Screw Extruder

Nanoreinforced™ iso-PP via Molecular Silicas™

<u>Imaging studies on Nanoreinforced™-PP fibers</u>

Molecular Silica™ dispersion confirmed at molecular level.

* Each "black dot" represents a 1.5nm POSS cage.



*scale of bar = 50nm

Viers - US Air Force Research Laboratory

Hybrid Plastics™

Mechanical Data on Me_8T_8/i-PP

Prof. Andre Lee - Michigan State University

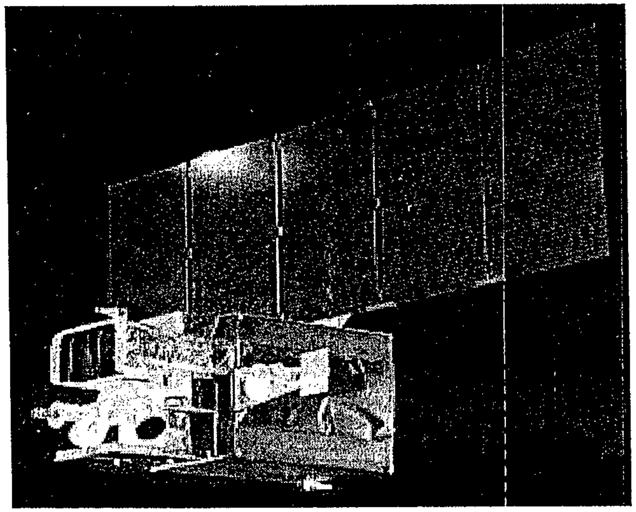
	Dow data	Neat *i*-PP (processed)	*i*-PP blended 2 wt% $Methyl_8T_8$	*i*-PP blended 5 wt% $Methyl_8T_8$	*i*-PP blended 10 wt% $Methyl_8T_8$
Tensile Strength @ Yield; ASTM D638	5000 psi (34.5 MPa)	4800 psi (33.0 MPa)	5000 psi (34.5 MPa)	5100 psi (35.1 MPa)	5200 psi (35.8 MPa)
Flexural Modulus (0.05 in/min, 1% secant); ASTM D790A	240,000 psi (1.655 GPa)	235,000 psi (1.620 GPa)	251,000 psi (1.730 GPa)	255,000 psi (1.757 GPa)	262,000 psi (1.80 GPa)
HDT @ 66 psi, as injected; ASTM D648	210 °F (99 °C)	210 °F (99 °C)	221 °F (105 °C)	239 °F (115 °C)	255 °F (124 °C)
Impact Izod @25C ASTM D256A	0.5 ft-lb/in	0.55 ft-lb/in	0.55 ft-lb/in	0.62 ft-lb/in	0.75 ft-lb/in

- **The above data (other than Dow's data) is an average of at least 10 samples for each test with acceptable S.D. of 5% or better.**

Summary: POSS-Polymer Blends

- The organic side groups on the POSS molecule are extremely important in determining the compatibility of the POSS in polymers
- In the case of Me_8T_8 (10%) in isotactic polypropylene, an increase in the Heat Distortion Temperature of 25 °C is observed
- Processing issues can be critical

POSS Application: Develop Multi-Functional, Space-Survivable Materials



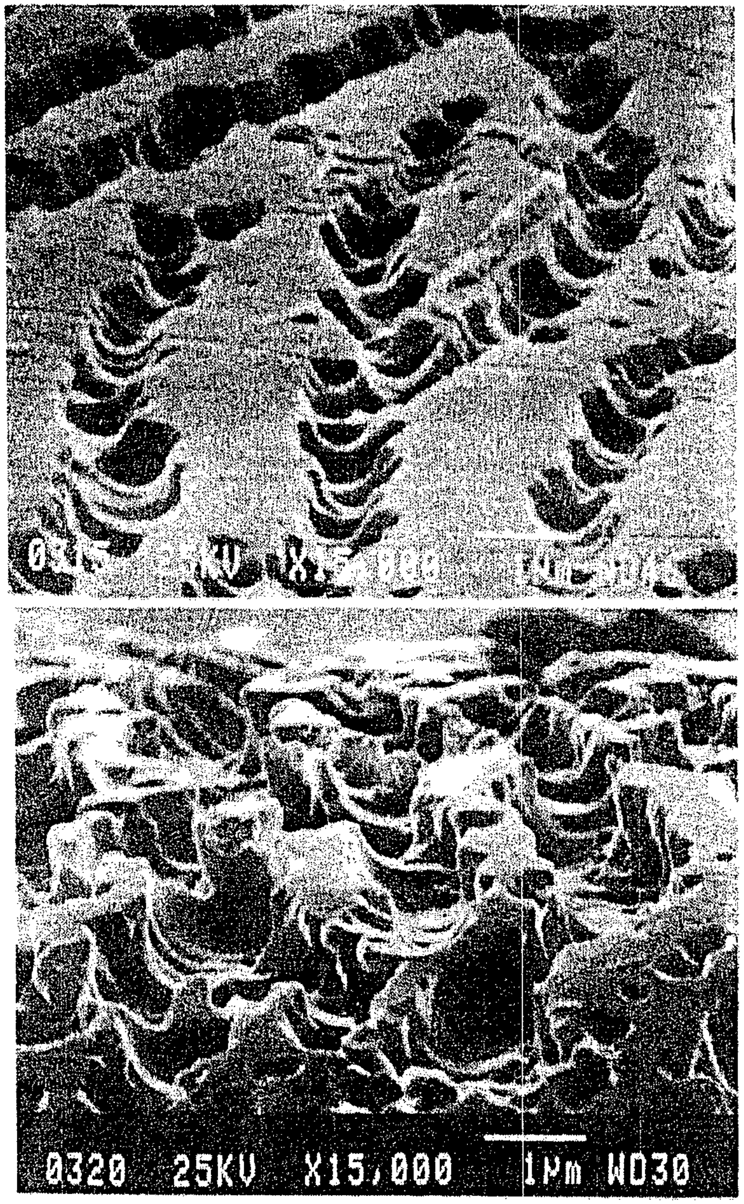
Satellites & Space Systems

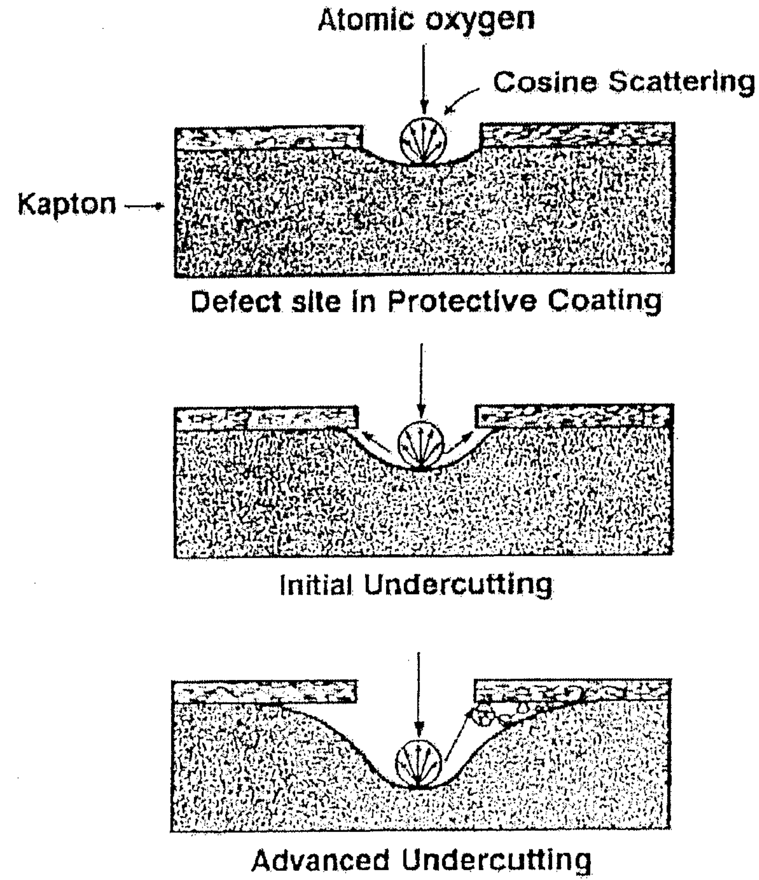
Bond	Dissociation Energy (EV)	λ (nm)	Material
$-C_6H_4-C(=O)-$	3.9	320	Kapton®
C-N	3.2	390	Kapton®
CF_3-CF_3	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

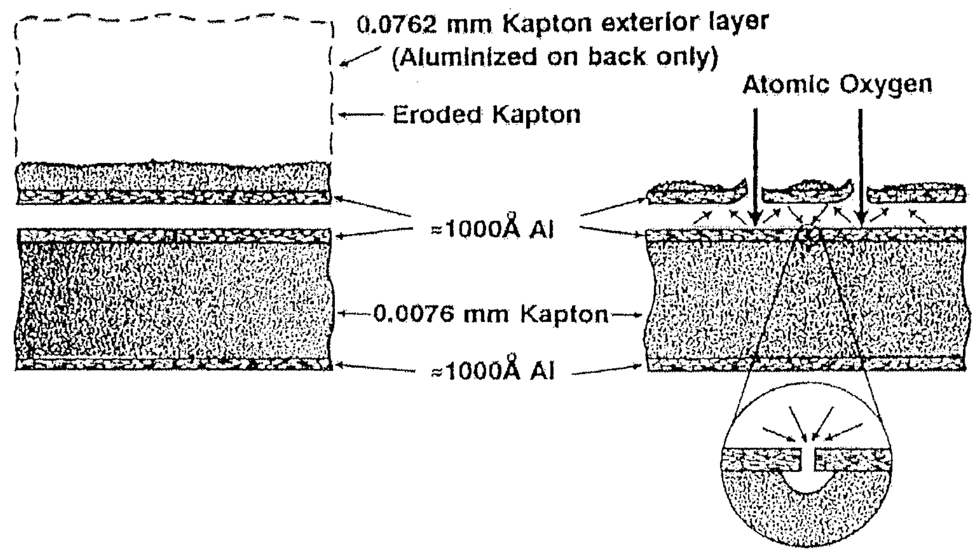
Objectives

- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials by 10x
- Self-Passivating/Self-Rigidizing/Self-Healing based on nanocomposite incorporation

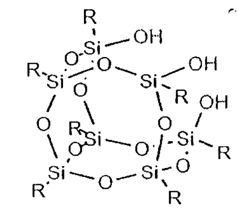
AO undercutting of LDEF Aluminized-Kapton Multilayer Insulation

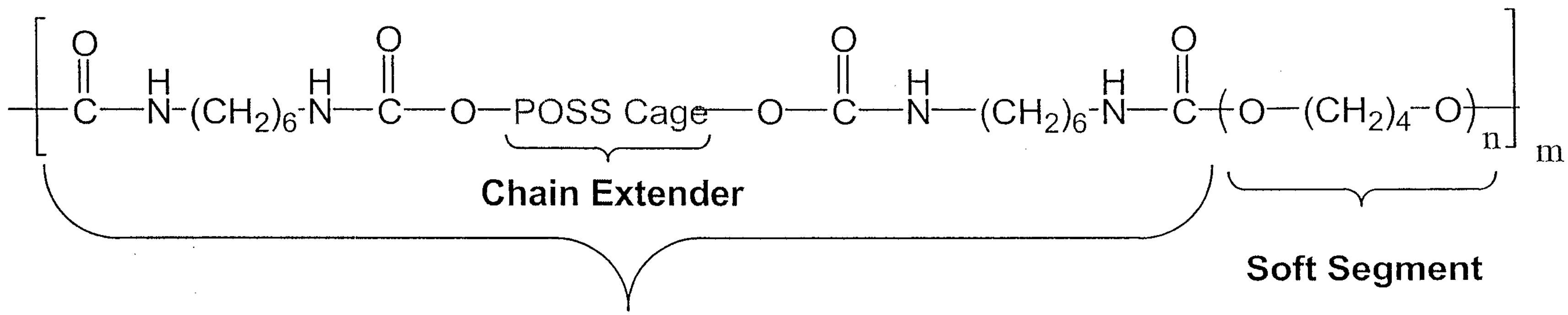






POSS-polyurethane Properties





POSS-polymer improvements

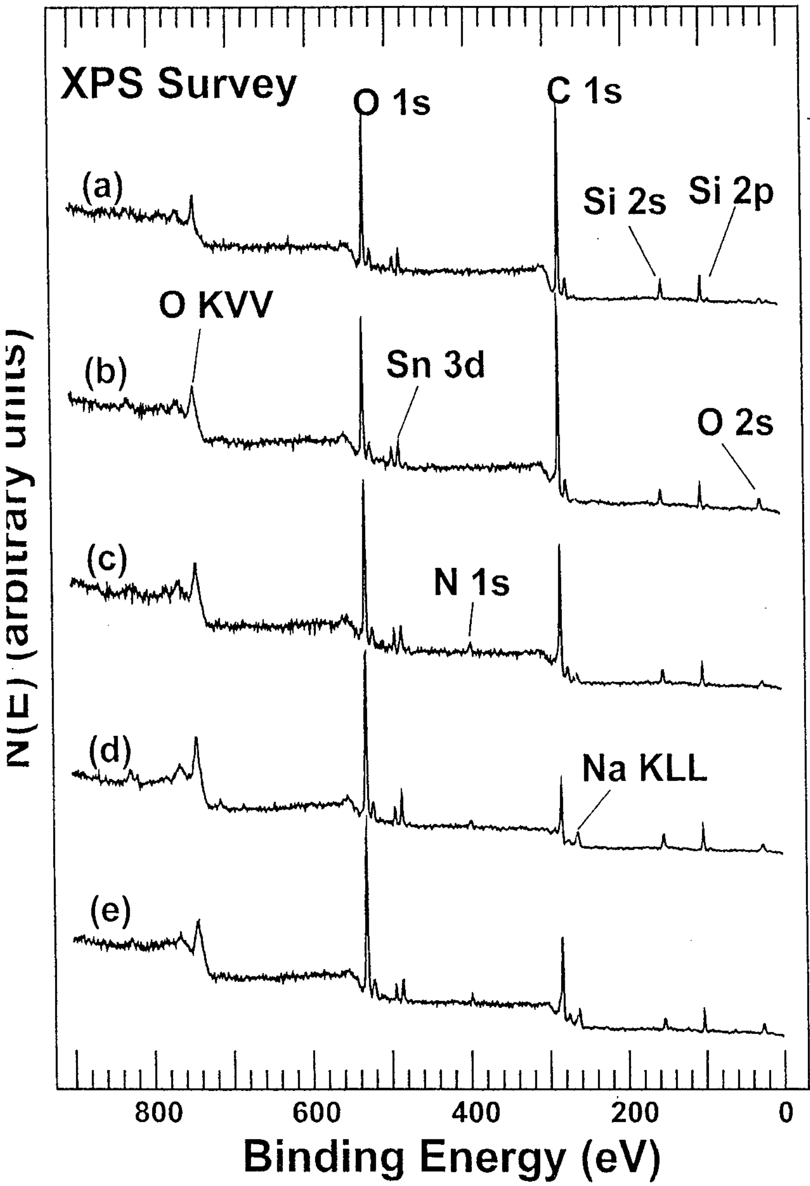
Up to 300 °C increase in the melt transition temperature (rheological studies show the transition from an oil to a true thermoplastic elastomer)

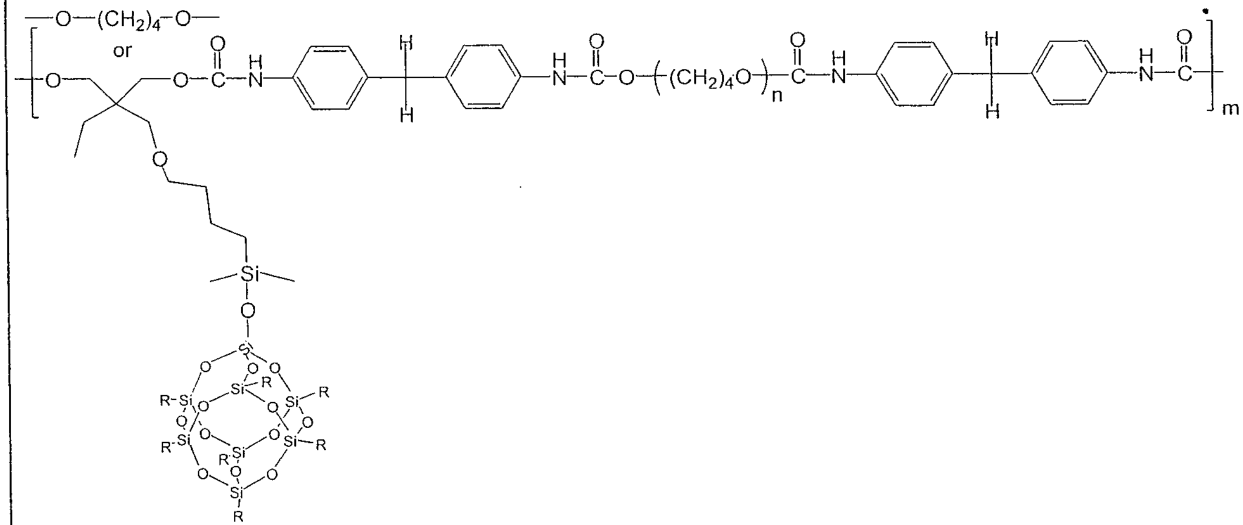
Up to a 100 °C increase in T_{dec} (29 wt% POSS, still TPE)

Up to 10X increase in moduli (>400% elongation with no destruction of hard segments))

17% POSS incorporation ----> 3X increase in Hardness (Shore A)

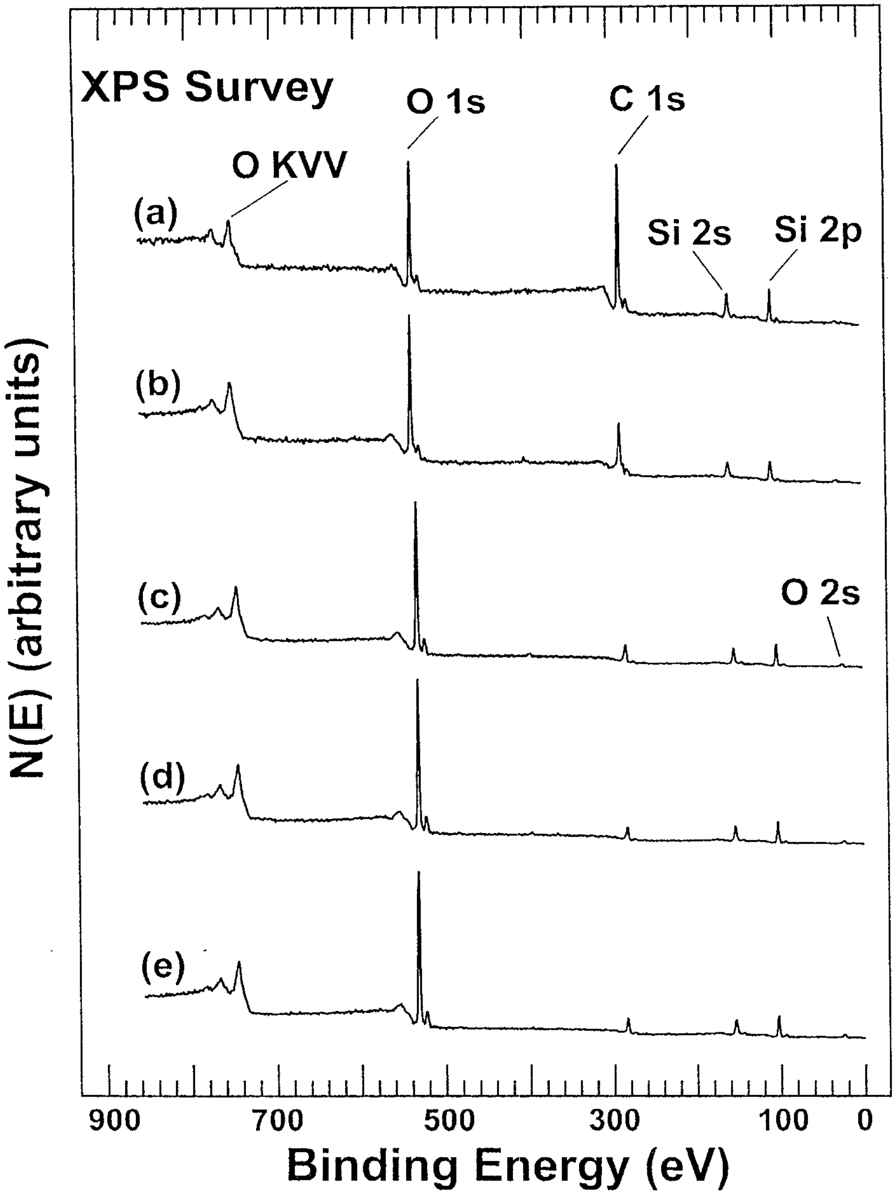
POSS Polyurethane



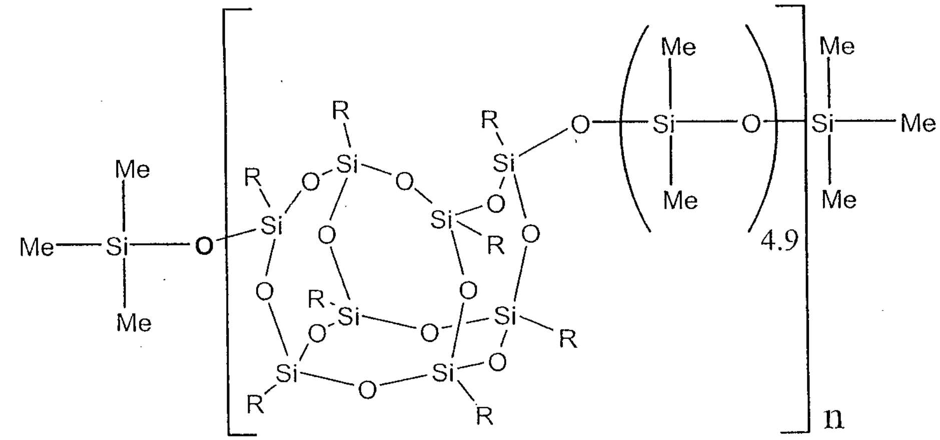


Sample Treatment	O	C	Si	Sn	Na	N
As entered	18.2	70.1	11.3	0.4	-	-
2.0-hr	17.5	70.2	11.2	0.7	0.4	-
24.0-hr	23.7	58.2	13.2	0.9	1.4	2.6
63.0-hr	35.3	37.3	20.4	1.3	3.0	2.7
3.3-h air	31.6	48.5	14.6	1.0	2.7	1.6

XPS Survey Spectra from a 60 wt% POSS-PU (a) after insertion into the vacuum system, (b) after a 2-hr (c) 24-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 3.3-hr air exposure following the 63-hr exposure.

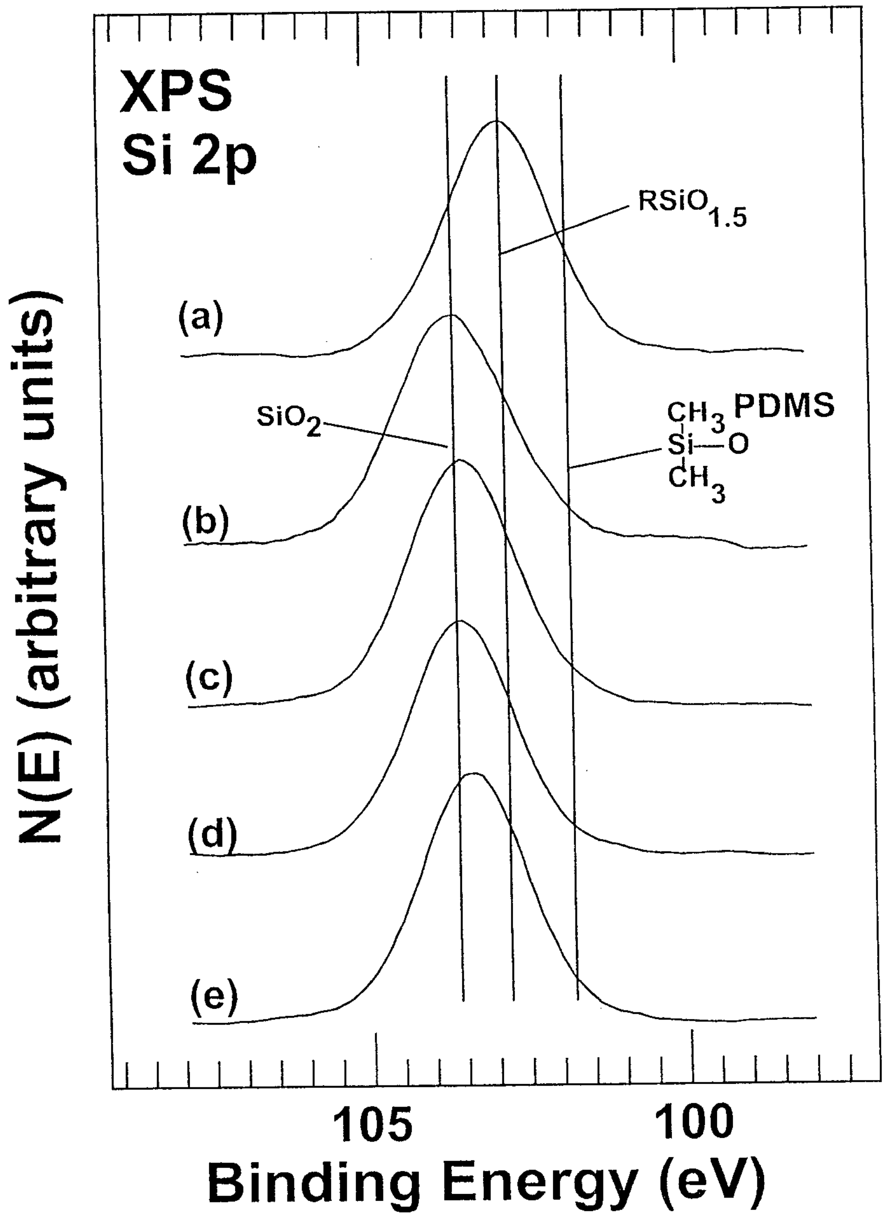


POSS Siloxane



Sample Treatment	O	C	Si
As entered	18.5	65.0	16.6
2.0 hr	33.8	48.4	17.8
24.6 hr	49.1	22.1	28.8
63.0 hr	55.7	16.3	28.0
4.8 hr air	52.8	19.5	27.7

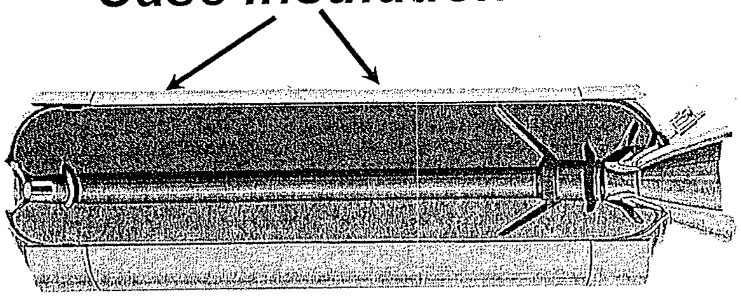
XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

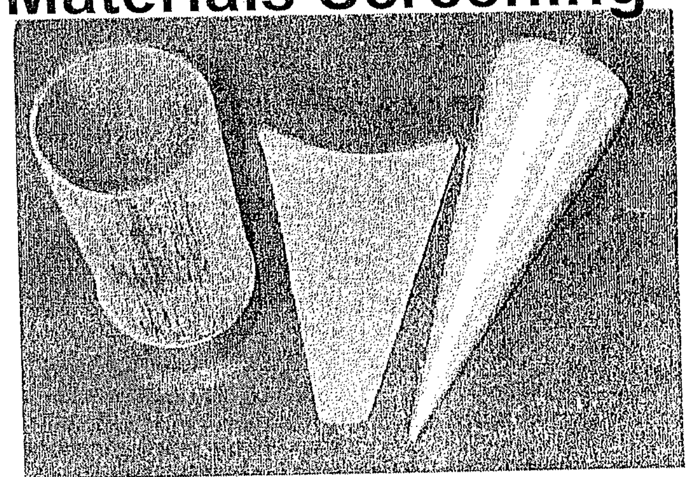


High Resolution Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

In-House SRM Insulation Testing

Low Cost/Low Volume Materials Screening





POSS-Insulation Sample

Goal: 50% Lower Erosion of Insulation (44 % weight reduction, 7.4% booster payload increase) – Phase III IHPRPT

Objective: Development of Ceramic Forming Polymer

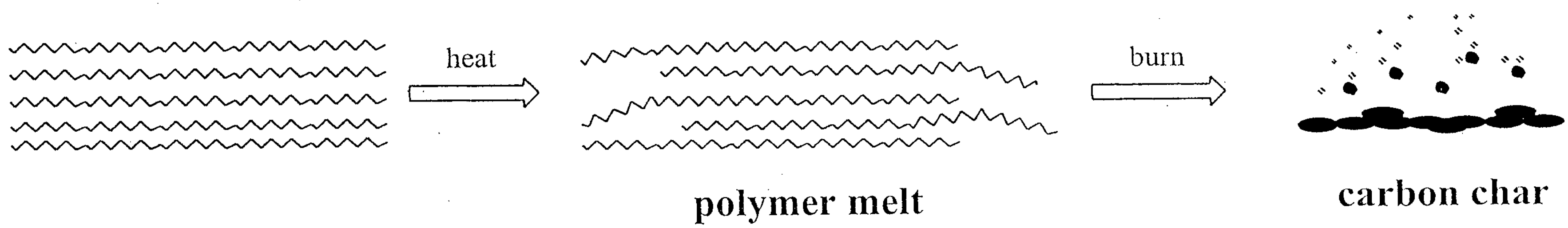
<u>POSS-Polymer Insulation - Advantages:</u>

- High loadings of POSS can be incorporated without embrittlement
- Si to O ratio is 1:1.5, proven to oxidize up to 1:2 (SiO_2)
- Tailorability of POSS monomers improve physical/mechanical properties
- Capabilities for Large and Small scale testing (Hybrid Plastics)

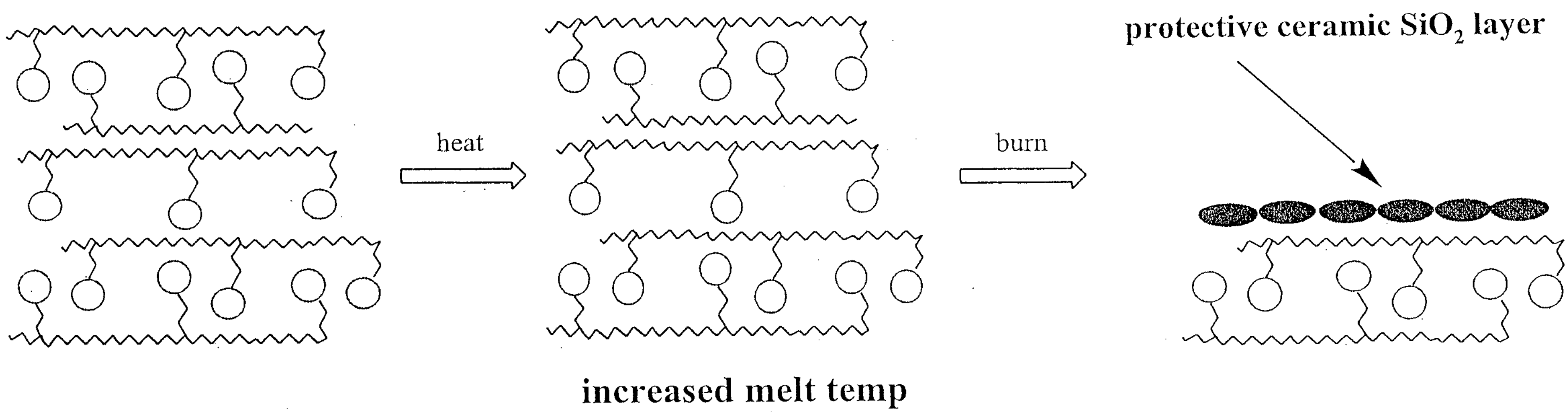
In-House SRM Insulation Testing

Formation of Silica Char Layer May lower ablation

Traditional Polymer



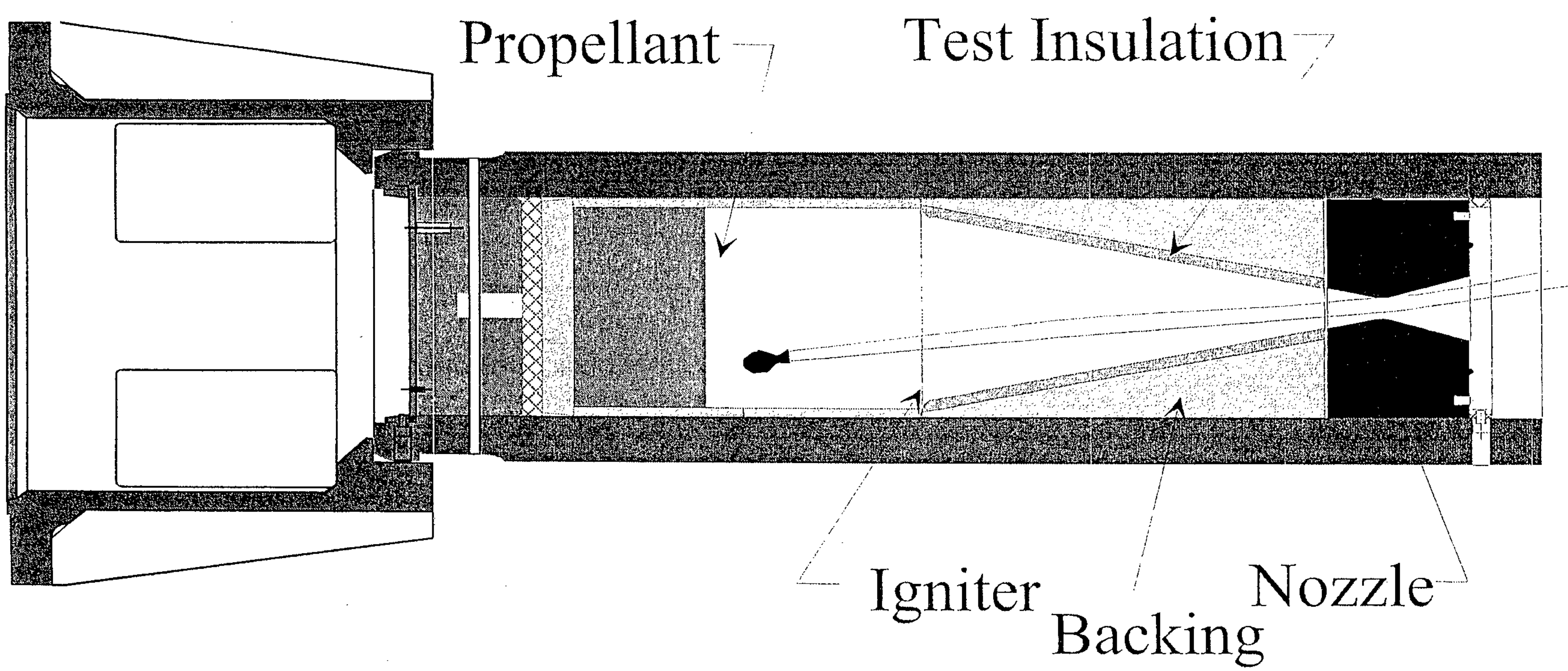
POSS Polymer



In-House SRM Insulation Testing
Low Cost/Low Volume Materials Screening

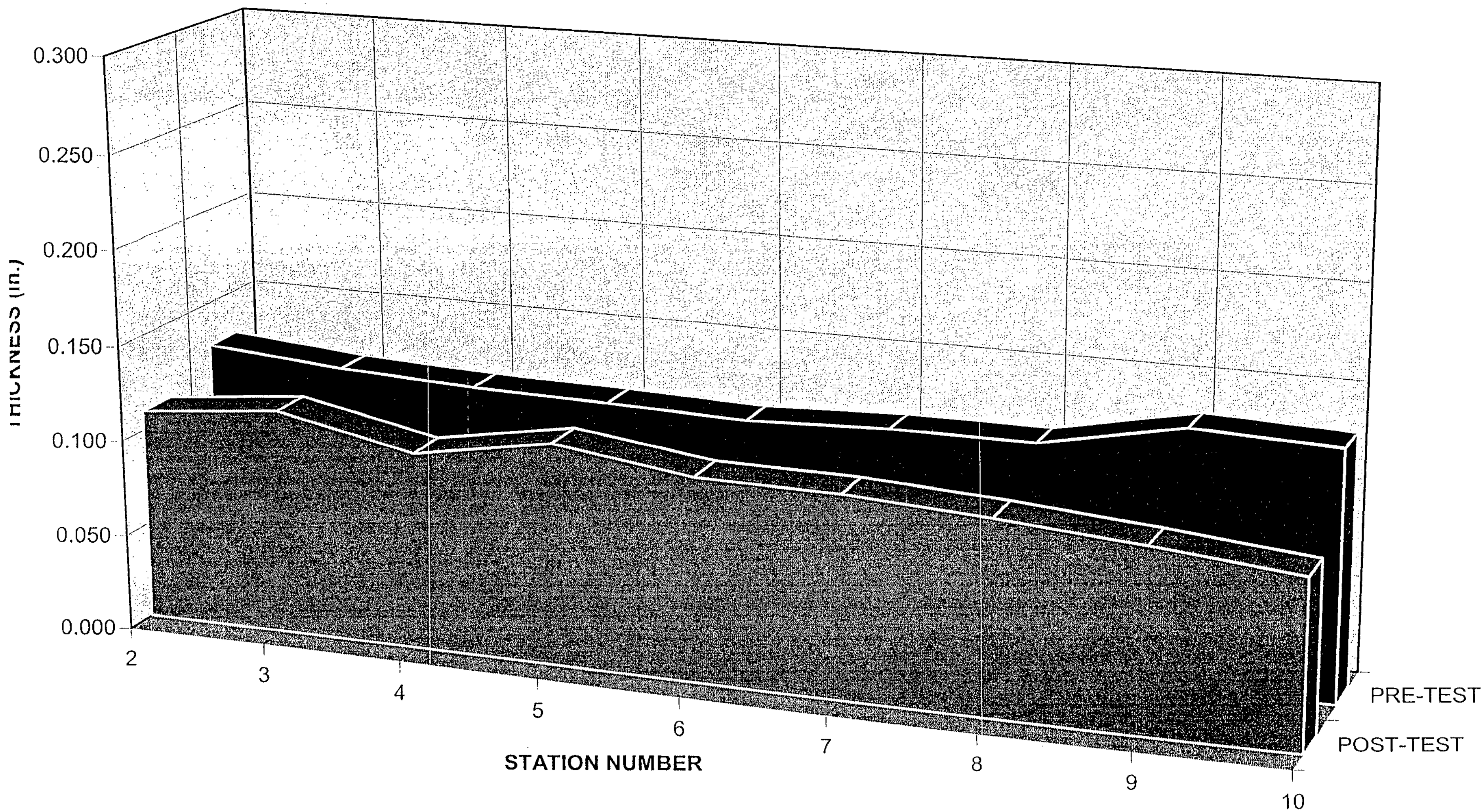
Capabilities:

- Edwards AFRL (4" Pi-K Motor): volume reduction (5 Kg to 75 g)
- Total Cost (synthesis, part fabrication, ablation test, analysis) ~ $1K
- Rapid testing of 5-6 samples per day



In-House SRM Insulation Testing
Low Cost Screening of New Materials

CHAR-063 ABLATION
(S10 - EPDM / Kevlar STANDARD)

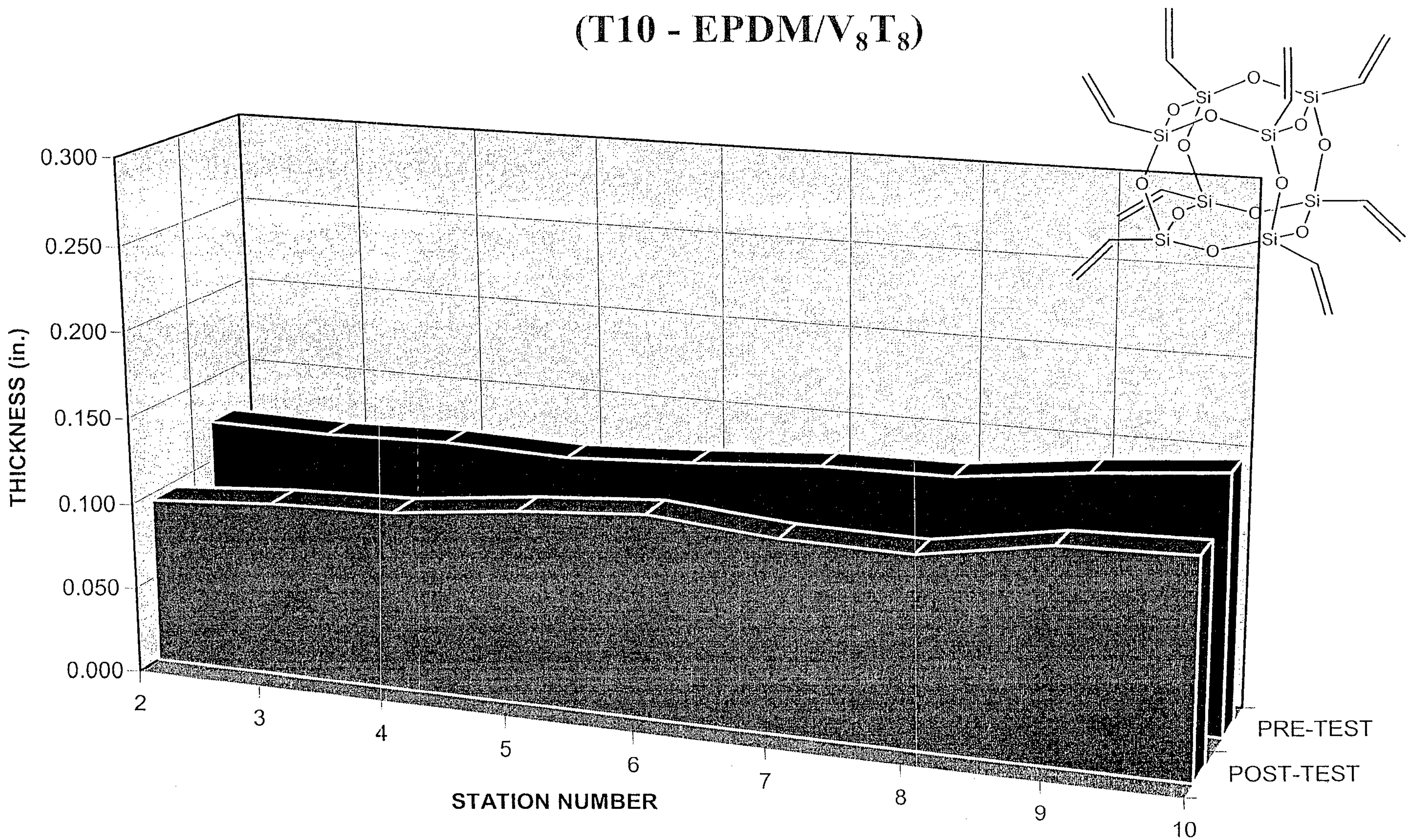


In-House SRM Insulation Testing

Low Cost Screening of New Materials

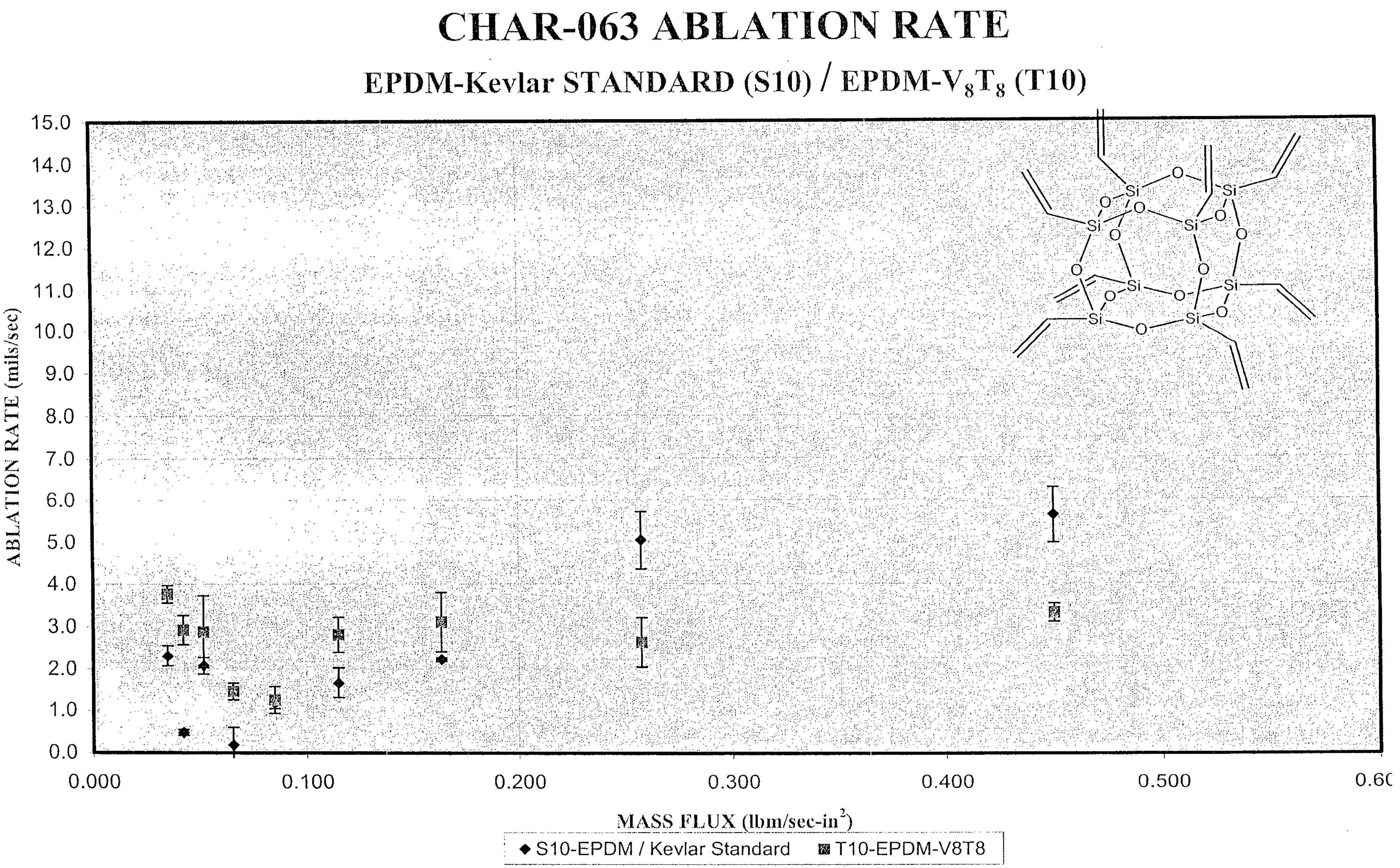
CHAR-063 ABLATION

(T10 - EPDM/V_8T_8)



In-House SRM Insulation Testing

Ablation Rate Decreased when Using POSS



Summary - Applications

- Demonstrated that POSS forms protective Silica layer when exposed to atomic oxygen in space-like conditions

- Initial evidence in SRM insulation tests suggests that POSS can act as an ablative in SRM insulation. Additional studies to confirm this are underway.

Programmatics: Dual Use & Leveraging

Polymer Working Group

Basic R&D → Processing → Applications R&D →

THE UNIVERSITY OF CALIFORNIA

AFRL/MLBP

MICHIGAN STATE UNIVERSITY

STONY BROOK
STATE UNIVERSITY OF NEW YORK

/PRPE

OHIO STATE

A United Technologies Company

UCONN

Plastics

IOWA STATE UNIVERSITY
Becoming the best.

UNIVERSITY OF FLORIDA

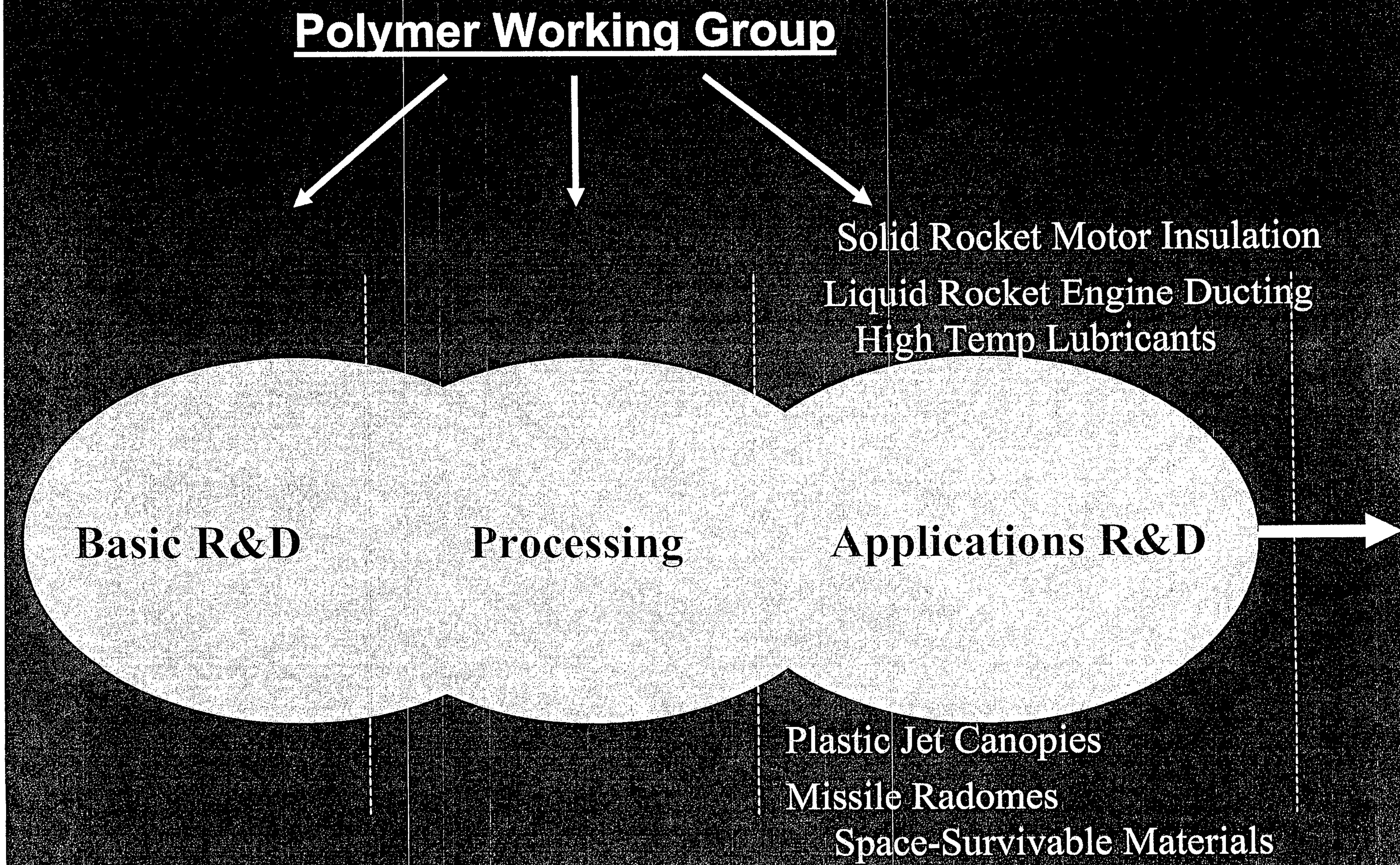
UMASS

UCSB

AFRL/MLBP

WTN
Wright Technology Network

Programmatics: Dual Use & Leveraging



CONCLUSIONS

Academic/Government Lab Collaborations are essential

Polymer Working Group

Basic R&D goal for controlling/understanding POSS affects on polymer properties is already ahead of schedule (including processing).

Cost, Volume and Production time goals have all been met thanks to Hybrid Plastics & Prof. Frank Feher.

Understanding processing is a key area that is being heavily worked.

POSS applications within government are on critical paths, while industrial interest has increased exponentially with technology transfer in 1998.